SUPPLEMENTARY INFORMATION OF

"Universal description of steric hindrance in flexible polymer gels"

1. FIGURE ILLUSTRATING THE BEAD-SPRING MODEL

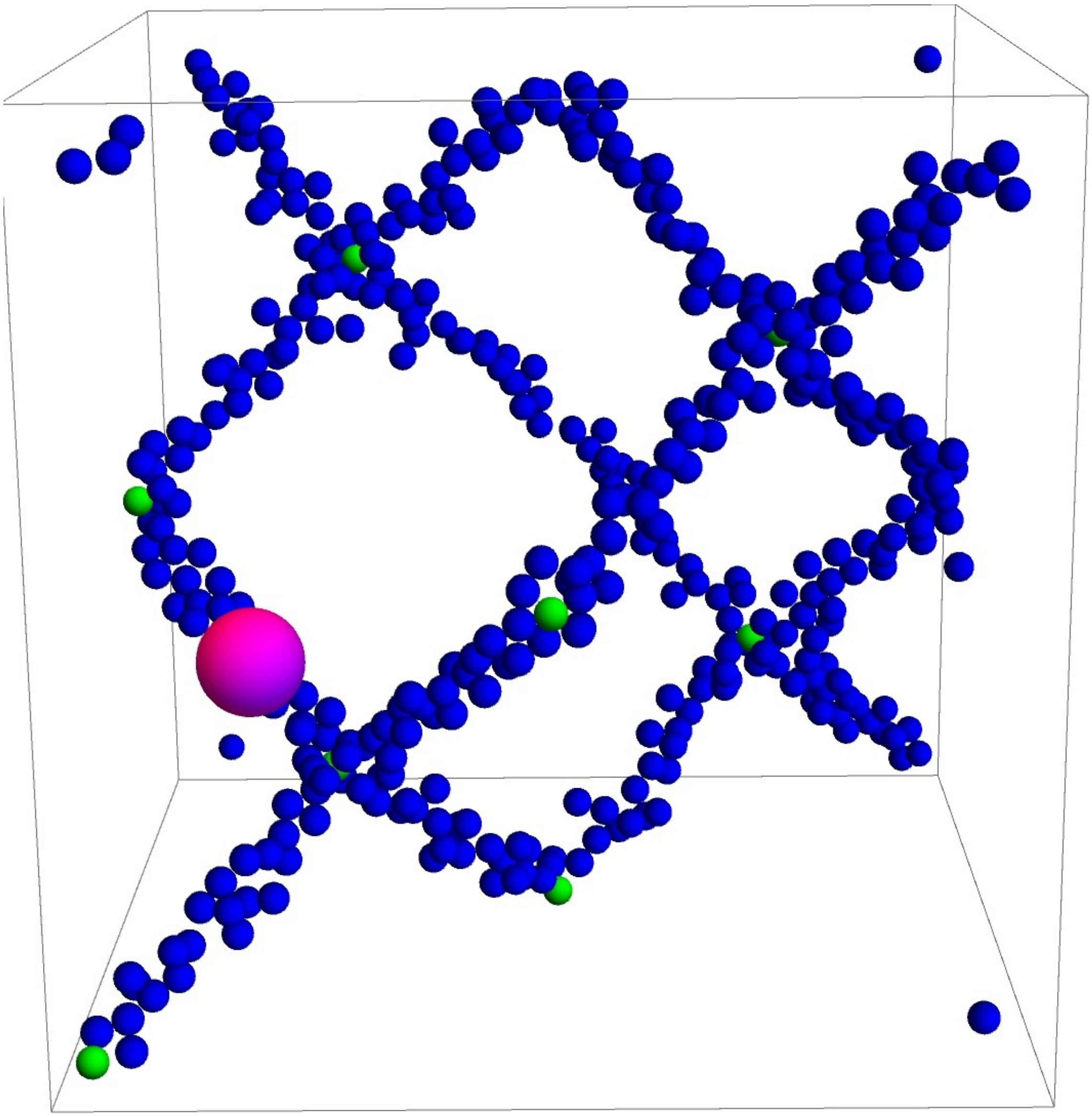

Figure SI-1. Snapshot of the simulation cell corresponding to a gel of 25 monomeric units per chain and a solute particle whose radius is 1 nm. Blue, green and magenta beads represent monomeric units, crosslinkers and solute particle, respectively. The simulation cell contains 8 crosslinkers.

2. EXAMPLE OF FIT PERFOMED TO OBTAIN DIFFUSION COEFFICIENTS.

Figure SI-2 shows an example of the fit performed to compute the diffusion coefficient of a solute particle with $R_s = 2.22$ nm diffusing in a hydrogel with $\varphi = 0.05$, $N_{mu} = 40$ and $k_e = 0.4$ N/m at 298 K. $\langle \Delta r^2 \rangle / 6t$ is plotted as a function of time and fitted to the exponential decay $D + Ae^{-t/\tau}$, where D, A and τ are adjustable parameters. D is the long-time diffusion coefficient.

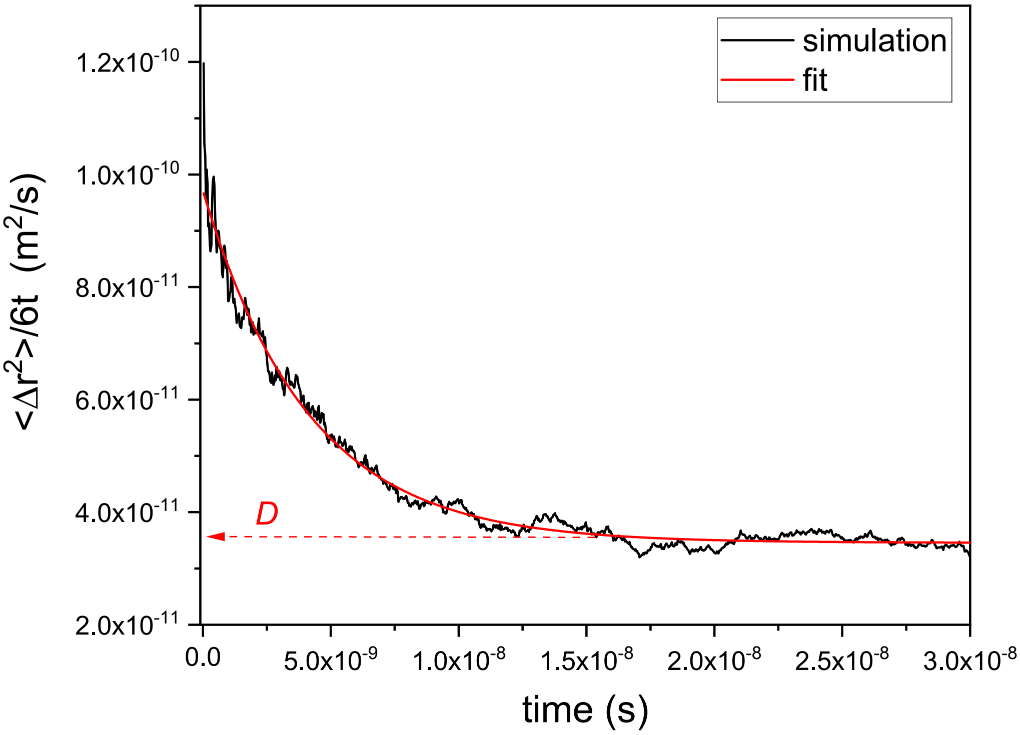

Figure SI-2. $\langle \Delta r^2 \rangle / 6t$ as a function of time for a solute particle with $R_s = 2.22$ nm diffusing in a hydrogel with $\varphi = 0.05$, $N_{mu} = 40$ and $k_e = 0.4$ N/m at 298 K. The black line represents the data obtained from simulation whereas the red line is the fit to an exponential decay. The arrow points to the value of the long-time diffusion coefficient on the *y*-axis.

It should be pointed out that $\langle \Delta r^2 \rangle / 6t$ is close to D_0 at very short times because the probability of finding polymer chains just at the beginning of a random walk is very small (particularly in the case of very low polymer volume fractions). In other words, a moderate-sized solute particle does not "see" the polymeric chains and its diffusive motion is apparently free. Only after some time, the Brownian motion of the solute is altered by the polymeric network and a stationary regime is reached.

3. ANOMALOUS DIFFUSION.

Figure SI-3 displays $\langle \Delta r^2 \rangle$ against t in log-log plot for the system of Figure SI-2. Three different regimes can be observed in this plot: two Brownian motions at short and long times ($\langle \Delta r^2 \rangle$ is proportional to t in both cases) and an intermediate region between them.

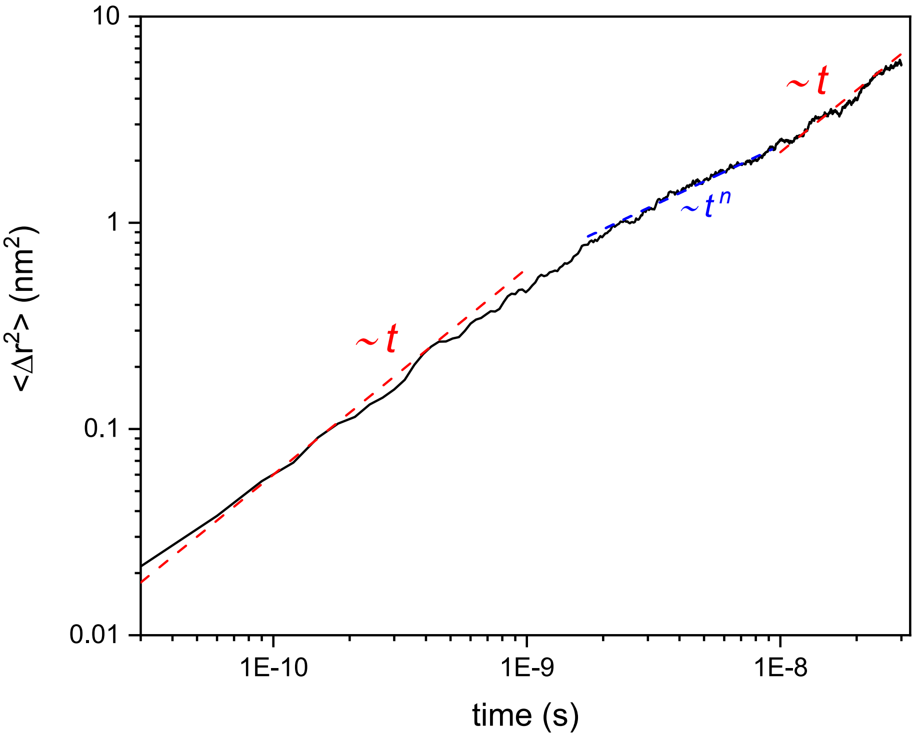

Figure SI-3. $\langle \Delta r^2 \rangle$ as a function of time for a solute particle with $R_s = 2.22$ nm diffusing in a hydrogel with $\varphi = 0.05$, $N_{mu} = 40$ and $k_e = 0.4$ N/m at 298 K. Red and blue dashed lines represent regions in which $\langle \Delta r^2 \rangle$ is proportional to t or t^n, respectively.

If $\langle \Delta r^2 \rangle$ is proportional to t^n (usually with $n < 1$) in this region, we say that this transient regime exhibits anomalous diffusion.[1–4] The exponent that characterizes this diffusive behavior (n) can be estimated by fitting the mean squared displacement (MSD) to an allometric function. In this study, however, we have followed the method proposed by Netz *et al.* for the estimation of n:[1] plotting $\log\left(\frac{\langle \Delta r^2 \rangle}{t}\right)$ against $\log(t)$. In this graph, the slope of the intermediate regime provides the value of $n - 1$. In any case, it should be stressed that the limits of this diffusive regime in time are not perfectly defined, which constitutes a source of uncertainty in n.

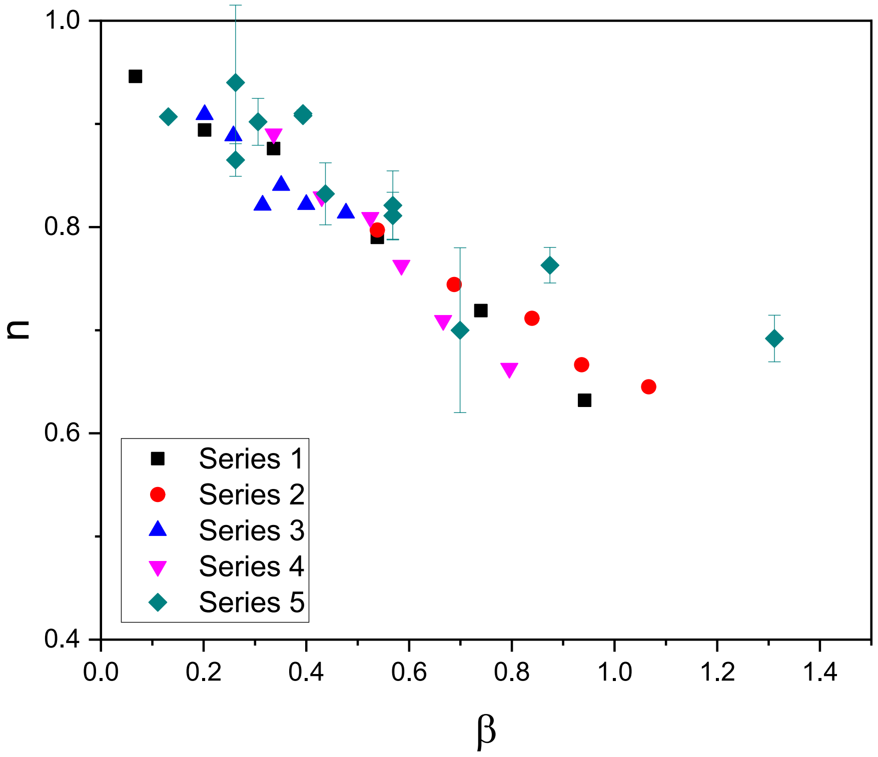

Figure SI-4. Exponent of anomalous diffusion (n) as a function of $\beta = \varphi(1 + R_s/R_m)^{1.3}$ for the five series of simulations carried out in this work.

Figure SI-4 shows the n-values obtained for the five series of simulations as a function of β. The error bars of Series 5 were computed from the fits performed by two of the authors. In this way, we exemplify the uncertainty caused by the subjective appreciation of the limits of the regime of anomalous diffusion. In some cases, this uncertainty can even be of the order of 0.08 and, consequently, care must be taken when drawing conclusions. In spite of this, the points of the five series appear to be distributed around a decreasing trend line when they plotted as a function of β, with the exception of the n-value corresponding to the highest polymer volume fraction of Series 5. This suggests that: i) β can also be a useful parameter in the description of anomalous diffusion of flexible polymer gels; ii) the exponent of anomalous diffusion decrease with the solute size and the polymer volume fraction.

4. RELATIVE DIFFUSIVITIES OF REAL SYSTEMS AS A FUNCTION OF α

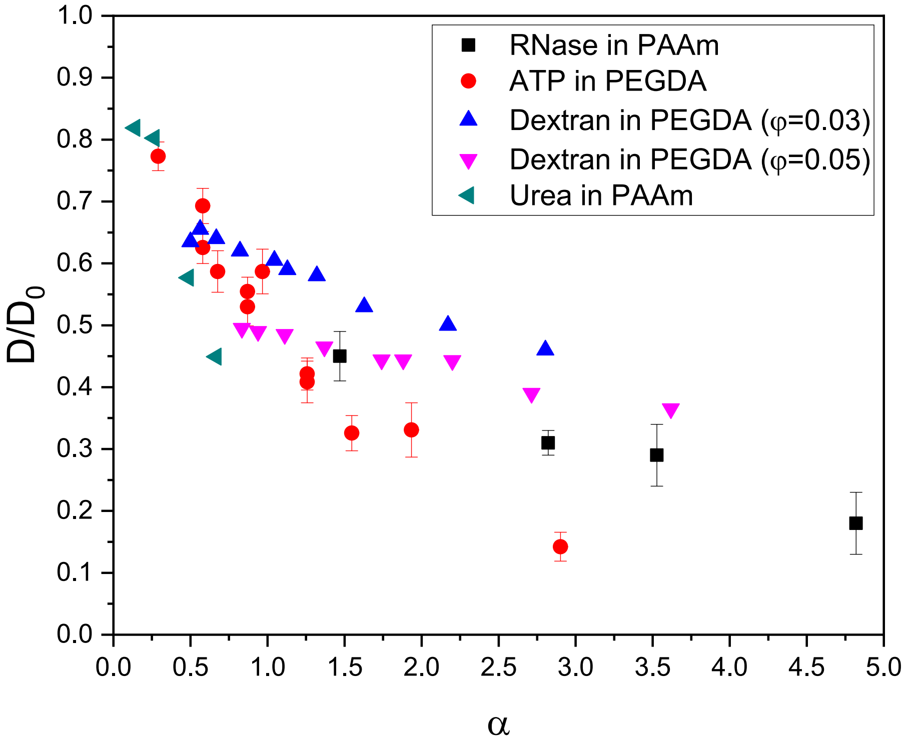

Figure SI-5. Relative diffusivity corresponding to real gel/solute systems as a function of $\alpha = \varphi(1 + R_s/R_m)^2$.

Figure SI-5 displays relative diffusivities of different real gel/solute systems as a function of parameter α. As can be easily inferred, these data do not collapse onto a master curve.

REFERENCES

1 P. A. Netz and T. Dorfmüller, Computer simulation studies of anomalous diffusion in gels: Structural properties and probe-size dependence, *J. Chem. Phys.*, 1995, **103**, 9074–9082.

2 R. Metzler, J. H. Jeon, A. G. Cherstvy and E. Barkai, Anomalous diffusion models and their properties: Non-stationarity, non-ergodicity, and ageing at the centenary of single particle tracking, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24128–24164.

3 S. K. Ghosh, A. G. Cherstvy and R. Metzler, Non-universal tracer diffusion in crowded media of non-inert obstacles, *Phys. Chem. Chem. Phys.*, 2015, **17**, 1847–1858.

4 A. G. Cherstvy, S. Thapa, C. E. Wagner and R. Metzler, Non-Gaussian, non-ergodic, and non-Fickian diffusion of tracers in mucin hydrogels, *Soft Matter*, 2019, **15**, 2526–2551.