# Diffusion and Release of Cargo from Collapsed Microgels: A Theoretical Framework

Adri Escañuela-Copado[1], José López-Molina[1], Matej Kanduč[2], Arturo Moncho-Jordá[1,3] and Irene Adroher-Benítez[1]

[1]Biocolloid and Fluid Physics Group, University of Granada, 18071 Granada, Spain

[2]Jožef Stefan Institute, SI-1000 Ljubljana, Slovenia

[3]Institute Carlos I for Theoretical and Computational Physics, 18071 Granada, Spain

Microgels are soft colloidal particles made of crosslinked polymer networks suspended in a liquid. Their size can be controlled by adjusting various factors, such as temperature. When the temperature of the liquid decreases, the polymer chains interact to increase their separation. The free volume inside each particle allows the microgels to absorb molecules. When the temperature rises, the polymers shrink, trapping the absorbed molecules in a dense mesh. This mesh enables the slow and controlled diffusion of the cargo molecules.

Previous studies have proposed a theoretical model that successfully predicts the molecule release kinetics of hollow microgels, as demonstrated in both simulations and experiments [1, 2]. However, this model fails to capture the behavior observed in dense homogeneous distributions of polymers. In this work, we aim to develop a theoretical framework that accurately describes the release of cargo from collapsed microgels. Diffusion through a dense polymer network has been shown to exhibit a different behavior from what is expected at lower polymer concentrations. The former process is governed by fluctuations happening in the microgel structure, while the latter is described by singular events of limited obstruction. This difference is the main reason for the discrepancy observed between the two scenarios [3].

In collapsed microgels, the spherical symmetry and high network density neutralize cargo-monomer interactions, except at the interface. This interface sets the boundary for the quasi-constant potential barrier, thereby making interactions crucial in determining the release time. The high concentration of polymers in collapsed microgels significantly restricts the movement of the cargo, leading to preferred diffusion directions dictated by the cargo's geometry. This situation has a notable effect over the diffusion coefficient and the depth of the potential barrier.

In this study, we have employed dynamical density functional theory (DDFT) to generate numerical results of the mean passage time for both repulsive and attractive microgels. This technique has been proven successful in previous works [1, 2]. These results have been accurately replicated by an analytic model, confirming the validity of our theoretical framework. Consequently, this work provides a robust and practical method for predicting the mean release time of anisotropic cargo from collapsed microgels.

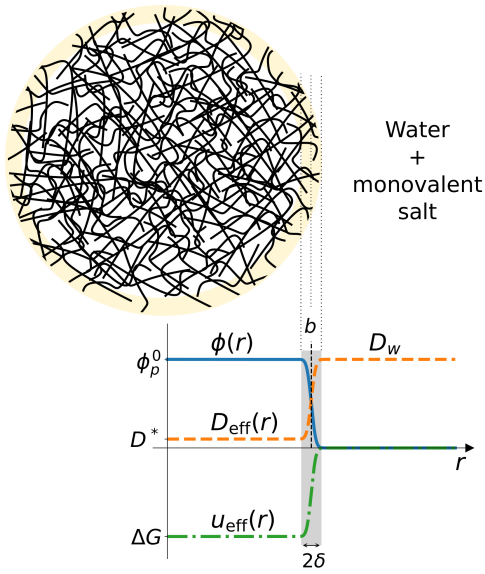


Fig. 1. Model of a collapsed microgel used in this study. The radius of the particle is denoted by $b$, and the interface width is $2\delta$. Three important system functions are illustrated: $\phi(r)$, representing the polymer packing fraction within the microgel; $D_{\text{eff}}(r)$, depicting the molecule effective diffusion coefficient which varies from $D^*$ inside the microgel to $D_{\text{w}}$ in bulk; and $u_{\text{eff}}(r)$, the effective microgel-molecule interaction, which assumes the value $\Delta G$ at the center of the colloidal particle.

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[2] A. Moncho-Jordá, A. B. Jódar-Reyes, M. Kanduč, A. Germán-Bellod, J. M. López-Romero, R. Contreras-Cáceres, F. Sarabia, M. García-Castro, H. A. Pérez-Ramírez, G. Odriozola, *Scaling Laws in the Diffusive Release of Neutral Cargo from Hollow Hydrogel Nanoparticles: Pacilataxel-Loaded Poly(4-vinylpyridine)*, ACS Nano **14**, 15227 (2020).

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