Responsive Microgels:
Connecting morphology, free energy and collective behaviour

A. Moncho Jordá[1,2], A. Cuetos[3], M. A. Fernández-Rodríguez[1], J. Dzubiella[4], A. Patti[1,2,5]

[1]Department of Applied Physics, University of Granada, Avenida Fuente Nueva s/n, 18071 Granada, Spain
[2]Carlos I Institute for Theoretical and Computational Physics, University of Granada, Av. Fuente Nueva s/n, 18071, Granada, Spain
[3]Department of Physical, Chemical and Natural Systems, Pablo Olavide University, Seville, Spain
[4]Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Germany
[5]Department of Chemical Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

INTRODUCTION

Core–shell microgels are soft, thermoresponsive particles whose internal architecture strongly influences their mechanical and collective behaviour [1]. Traditional models often neglect the heterogeneity between the dense core and softer shell, limiting predictions under compression [2,3]. Here, we develop a coarse-grained framework that captures the distinct mechanical properties of core and shell regions, enabling self-consistent modelling of **swelling**, **compressibility**, and particle–particle **interactions**. This approach provides a foundation to understand how particle **softness** and **internal structure** govern the phase behaviour and microstructure of concentrated microgel suspensions [4].

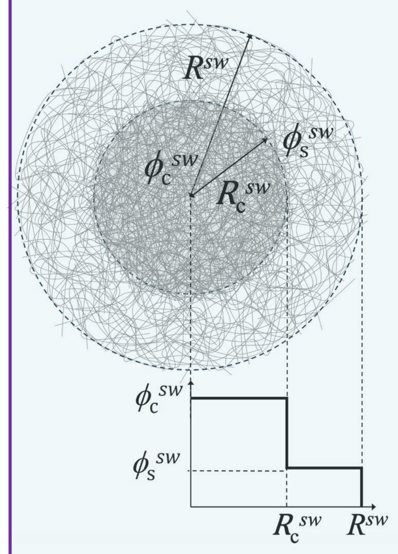
OBJECTIVES

- Developing a coarse-grained framework that **distinguishes core and shell** contributions to microgel mechanics
- Modelling swelling, compressibility, and internal mechanical equilibrium under thermal and mechanical **stimuli**.
- Implementing a **responsive** multi-Hertzian pair potential to capture particle–particle **interactions** in concentrated suspensions.
- Investigating how particle-level **heterogeneity** and **softness** influence microstructure, packing, and phase behaviour.

THEORY

Polymer distribution of a swollen microgel

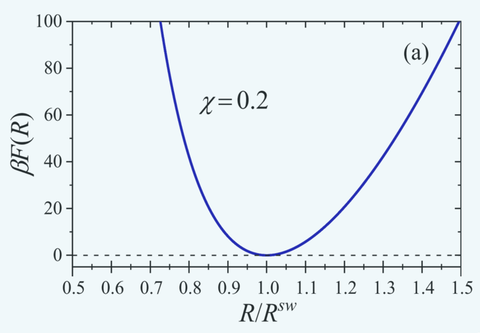
$$\phi_c^{sw} = \frac{3\upsilon_{mon}}{(R_c^{sw})^3}\int_0^{R_c^{sw}} r^2\rho(r)\mathrm{d}r = \rho_c^{sw}\upsilon_{mon} \qquad n_i = \left(\frac{k}{\phi_i^{sw}}\right)^{5/4} \qquad i = \mathrm{c,\ s}$$



$$\phi_s^{sw} = \frac{3\upsilon_{mon}}{(R^{sw})^3-(R_c^{sw})^3}\int_{R_c^{sw}}^{R^{sw}} r^2\rho(r)\mathrm{d}r$$
$$= \frac{1}{10}\frac{\phi_c^{sw}}{(R^{sw})^3-(R_c^{sw})^3}[(R^{sw})^3 + (R^{sw})^2(R_m + R_c^{sw}) + R^{sw}(R_m^2 + R_m R_c^{sw} + (R_c^{sw})^2) + R_m^3 + R_m^2 R_c^{sw} + R_m(R_c^{sw})^2 - 9(R_c^{sw})^3]$$

Free energy

Within the Flory-Rehner theory, the intrinsic free energy of the microgel is split into three additive contributions: elastic, solvent-induced and ionic free-energy terms



$$F_i(\phi_i) = N_{ch,i}k_BT\left[\underbrace{\frac{3}{2}\left(\left(\frac{\phi_{0i}}{\phi_i}\right)^{2/3} - \ln\left(\frac{\phi_{0i}}{\phi_i}\right)^{1/3} - 1\right)}_{F_{elastic}} + \underbrace{\ln\phi_i + n_iB\left(\frac{1}{\phi_i}-1\right)\ln(1-\phi_i) + n_iB\chi(1-\phi_i)}_{F_{solvent}} + \underbrace{f_i\ln\left(\frac{\phi_i}{\phi_{0i}}\right)}_{F_{ion}}\right]$$

Mechanical Properties of Compressed Microgels

$\Pi_c(\phi_c) = \Pi_s(\phi_s)$ mechanical equilibrium

$$\Pi_i = -(1/v_{solv})(\partial F_i/\partial N_{solv})_T \ (i = \mathrm{c,\ s})$$

$$\Rightarrow \begin{cases} R_c = R_c^{sw}\left(\dfrac{\phi_c^{sw}}{\phi_c}\right)^{1/3} \\ R = \left[R_c^3 + \dfrac{\phi_s^{sw}}{\phi_s}((R^{sw})^3 - (R_c^{sw})^3)\right]^{1/3} \end{cases}$$

$$K_i(\phi_i) = \phi_i\left(\frac{\partial\Pi_i}{\partial\phi_i}\right)_T \qquad Y_i(R) \approx \frac{3}{2}k_BT\frac{N_{ch,i}}{V_i} \qquad \sigma_i(\phi_i) = \frac{3K_i - Y_i}{6K_i}$$

Bulk modulus — *Young modulus* — *Poisson's ratio*

Pair interaction between core-shell microgels

$$u(r) = u_{cc}(r;\, R_c, R_c') + u_{cs}(r;\, R_c, R_s') + u_{sc}(r;\, R_s, R_c') + u_{ss}(r;\, R_s, R_s')$$

$$\beta u_{ij}(r;\, R_i, R_j') = \epsilon_{ij}(R_i, R_j')\left(1 - \frac{r}{R_i + R_j'}\right)^{5/2}\theta(R_i + R_j' - r)$$

$$\epsilon_{ij}(R_i, R_j') = \frac{8C}{15k_BT}A_{eff,ij}(R_i + R_j')^2(R_iR_j')^{1/2} \quad i, j = \mathrm{c,\ s}$$

SIMULATION

Simulation Setup

- Monte Carlo (MC) simulations in NPT ensemble
- Cubic box with periodic boundaries
- N = 1000 spherical particles
- Interaction: *multi-Hertzian potential*
- Conditions:
  - $T^* = T/T_{LCST} = 0.9487$
  - $P^* = 8(R_{sw})^3P/(k_BT_{LCST}) = 0.05\text{–}13{,}000$

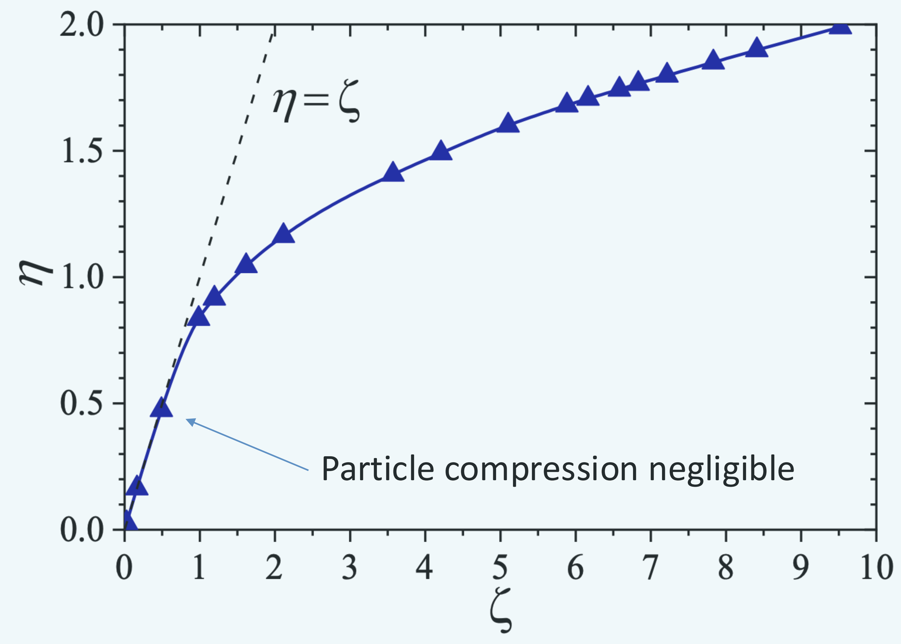
Simulation Procedure

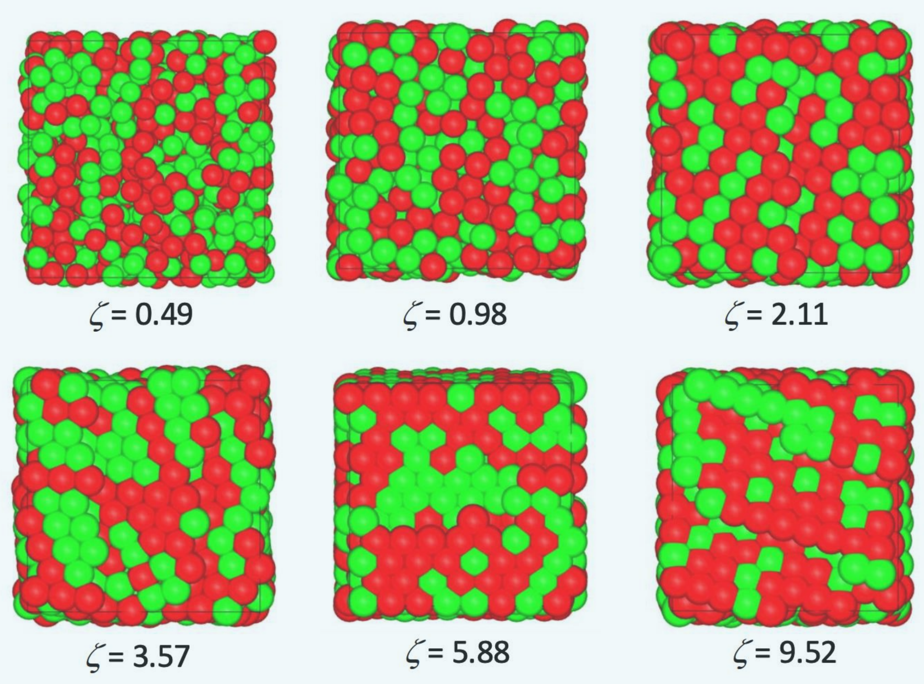
- Each MC cycle: *N* trial moves
- Random particle:
  - **Displaced** $(r \to r + \Delta r)$
  - **Resized** $(R \to R + \Delta R)$
- **Box volume change:** $(V_T \to V_T + \Delta V)$
- **Move probabilities:**
  - 80% displacement
  - 20% size change

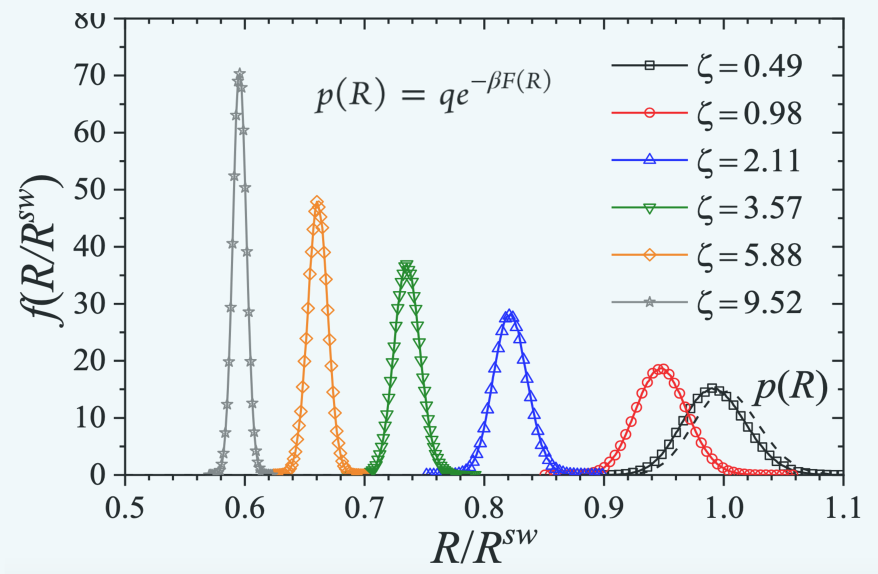
Volume Fractions

- **The nominal volume fraction** ζ
  - **Is the volume fraction** if all particles were fully **swolle**
  - Based on the **parent size distribution** $p(R)$
- The **effective volume fraction** η
  - Reflects **instantaneous particle sizes**
  - Captures the system's **size polydispersity**

$$\zeta = \frac{4}{3}\pi\frac{N}{V_T}\int R^3p(R)\mathrm{d}R \qquad \eta = \frac{4}{3}\pi\frac{N}{V_T}\int R^3f(R)\mathrm{d}R$$

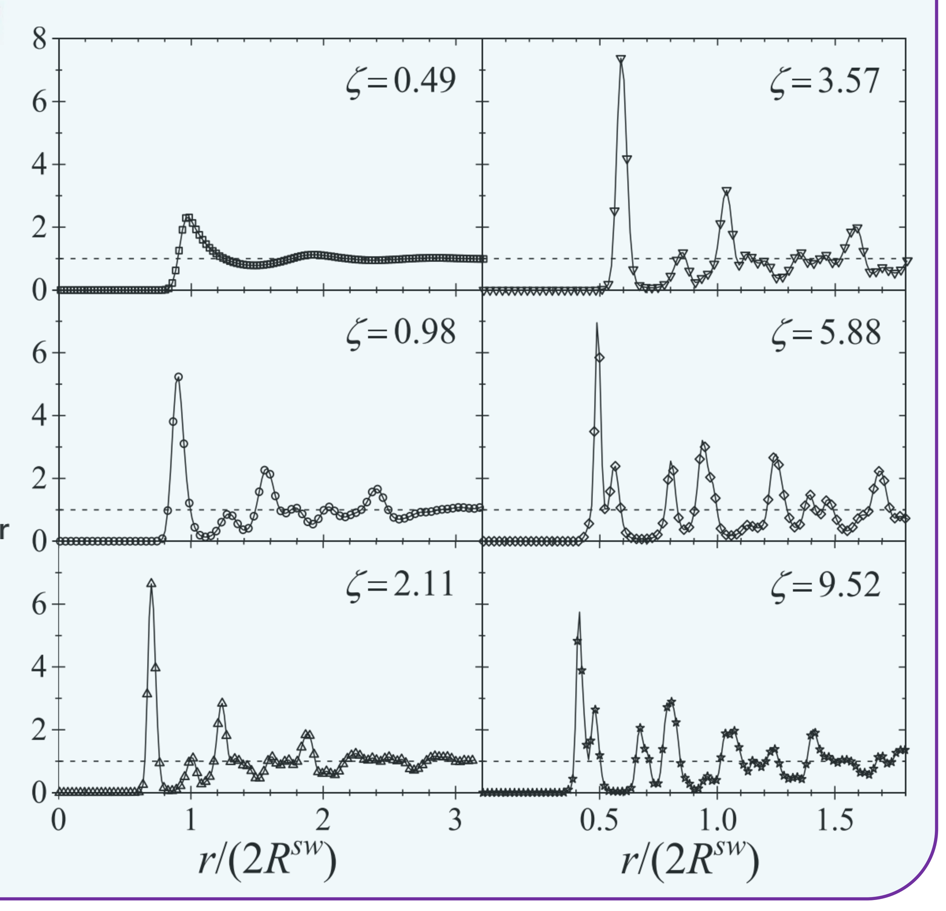






Crystalline Order at Different Volume Fractions

- **Intermediate volume fractions:**
  - **Mixed HCP and FCC domains with defects**
  - Example at $\zeta = \mathbf{3.57}$:
    - **~47%** of particles in **HCP** environments
    - **~41%** in **FCC** environments
    - **<1%** in **BCC** environments
    - Remaining particles show **no identifiable crystalline order**
- **Higher volume fractions:**
  - $\zeta = \mathbf{5.88}$ and $\zeta = \mathbf{9.52}$
  - **>80%** of particles adopt **BCC** environments
  - Remaining particles mostly **disordered**
  - Negligible fraction exhibits **HCP** or **FCC** order



CONCLUSIONS

We developed a coarse-grained framework capturing the heterogeneous **core–shell structure** and **mechanical response** of microgels, enabling self-consistent modeling of **swelling, compressibility, and particle interactions**. Simulations with a **responsive multi-Hertzian potential** reproduce key features of concentrated suspensions, including **size distribution evolution, effective packing fraction, and structural correlations**. Our results show that **particle-level softness and internal heterogeneity** critically govern collective behavior and phase transitions, highlighting the need for models beyond **fixed-shape or single-modulus descriptions**. This framework provides a versatile basis for studying microgels under **confinement, crowding, or external stimuli** and can extend to **interfacial or multicomponent systems**.

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e-mail: moncho@ugr.es – apatti@ugr.es