

## In Silico Synthesis of Microgel Particles

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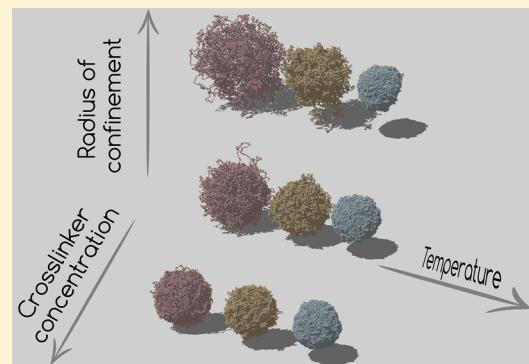
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**ABSTRACT:** Microgels are colloidal-scale particles individually made of cross-linked polymer networks that can swell and deswell in response to external stimuli, such as changes to temperature or pH. Despite a large amount of experimental activities on microgels, a proper theoretical description based on individual particle properties is still missing due to the complexity of the particles. To go one step further, here we propose a novel methodology to assemble realistic microgel particles *in silico*. We exploit the self-assembly of a binary mixture composed of tetravalent (cross-linkers) and bivalent (monomer beads) patchy particles under spherical confinement in order to produce fully bonded networks. The resulting structure is then used to generate the initial microgel configuration, which is subsequently simulated with a bead–spring model complemented by a temperature-induced hydrophobic attraction.

To validate our assembly protocol, we focus on a small microgel test case and show that we can reproduce the experimental swelling curve by appropriately tuning the confining sphere radius, something that would not be possible with less sophisticated assembly methodologies, e.g., in the case of networks generated from an underlying crystal structure. We further investigate the structure (in reciprocal and real space) and the swelling curves of microgels as a function of temperature, finding that our results are well described by the widely used fuzzy sphere model. This is a first step toward a realistic modeling of microgel particles, which will pave the way for a careful assessment of their elastic properties and effective interactions.



### I. INTRODUCTION

Soft colloids, combining properties of hard-sphere colloids and polymers, offer the interesting possibility to tailor their macroscopic behavior and flow at the molecular level.<sup>1</sup> Hard sphere colloids have served for decades as a reference model to shed light on many physics problems, such as the structure of atomic liquids,<sup>2</sup> crystal nucleation,<sup>3</sup> and the glass transition.<sup>4–6</sup> Recently, however, soft colloids have become even more popular in the scientific community.<sup>7</sup> Typically, soft particles have an internal polymeric architecture, which allows them to reach the paste regime,<sup>8</sup> where particles are in very dense, squeezed (or jammed) states. Under such conditions, the polymeric chains experience a substantial interpenetration,<sup>9</sup> and the internal structure of particles themselves changes. Since the single-particle elasticity alters the properties of the resulting macroscopic material, establishing the crucial link between microscopic properties and macroscopic response requires the knowledge of the effective interactions among particles. Yet, while synthesis and experiments have produced an immense database of soft polymeric colloids,<sup>1</sup> theoretical efforts still lag behind. The most dramatic example of such a dichotomy is offered by microgels, which are soft particles with tunable swelling properties and an extremely broad range of materials applications. Microgels are nano- or microsized particles made by cross-linked polymer networks, which can respond to external stimuli, such as changes to temperature  $T$  or pH, by swelling and deswelling (on a short time scale as compared to

macrogels). The important experimental advantage of using microgels as a model system is that, thanks to the aforementioned responsiveness, the size of the particles can be finely controlled. Such a sensitivity is usually exploited to carefully tune the sample volume fraction without changing the particle number density. This property allows to explore classical physics problems from new points of view: for example, by using confocal microscopy, it is possible to follow the melting of colloidal crystals by tuning the temperature, allowing to investigate fluidization events at grain boundaries<sup>10</sup> or to study the nature of the fluid–hexatic–crystal transition in 2D.<sup>11</sup> Similarly, a slow annealing induces a reversible assembly of crystals even in the presence of defects,<sup>12</sup> while size changes can be used to smartly vary the lattice spacing and to obtain color-tunable crystals.<sup>13</sup>

Among microgels, largely studied are those based on PNIPAM cross-linked networks, which are thermoresponsive and display a volume phase transition (VPT) at  $T \sim 32\text{ }^{\circ}\text{C}$ , from a swollen state at low  $T$  to a compact state at high  $T$ . The first synthesis of PNIPAM microgels in 1986<sup>14</sup> was followed by hundreds of publications, including several reviews on synthesis,<sup>15,16</sup> applications,<sup>17,18</sup> and physical aspects<sup>7,19</sup> as well as several books.<sup>20–22</sup> Despite microgels being one of the most

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