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Theory of the Thermal Diffusion of Microgel Particles in Highly Compressed Suspensions JEFFREY SOKOLOFF, Retired, CRAIG MALONEY, Northeastern University, MASSIMO CIAMARRA, NTU, Singapore, DAPENG BI, Northeastern University — One amazing property of microgel colloids is the ability of the particles to thermally diffuse, even when they are compressed to a volume well below their swollen state volume, despite the fact that they are surrounded by and pressed against other particles. A glass transition is expected to occur when the colloid is sufficiently compressed for diffusion to cease. It is proposed that the diffusion is due to the ability of the highly compressed particles to change shape with little cost in free energy. It will be shown that most of the free energy required to compress microgel particles is due to osmotic pressure resulting from either counterions or monomers inside of the gel, which depends on the particle's volume. There is still, however, a cost in free energy due to polymer elasticity when particles undergo the distortions necessary for them to move around each other as they diffuse through the compressed colloid, even if it occurs at constant volume. Using a scaling theory based on simple models for the linking of polymers belonging to the microgel particles, we examine the conditions under which the cost in free energy needed for a particle to diffuse is smaller than or comparable to thermal energy, which is a necessary condition for particle diffusion. Based on our scaling theory, we predict that thermally activated diffusion should be possible when the mean number of links along the axis along which a distortion occurs is much larger than $N^{1/5}$, where $N$is the mean number of monomers in a polymer chain connecting two links in the gel.

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