The nature of anisotropic particles with short-range interactions

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Anisotropic particles are used widely to control the thermodynamic and rheological properties of pharmaceuticals, cosmetics, food products, composite materials, and cements. In particular, rod-like particle suspensions exhibit unique equilibrium and non-equilibrium states at low particle loadings due to large excluded volumes and orientation-dependent attractions. However, the coupled effects of particle shape and interactions are not quantitatively understood with regard to dynamically arrested states, such as colloidal gels and glasses. To better quantify these coupled effects, a tunable model system of adhesive hard rods (AHR) was synthesized to independently control the particle aspect ratio and the temperature-dependent, short-range attractions. AHR suspensions were composed of octadecyl-coated silica rods suspended in tetradecane, which displayed thermoreversible dynamic arrest transitions. The dynamic moduli and particle dynamics were quantified systematically using macroscopic rheological methods and microscopic quasi-elastic light scattering methods, providing a quantitative map of the gel and glass boundaries as a function of aspect ratio (L/D 3 to 7), particle volume fraction (φ 0.1 to 0.5), and absolute critical temperatures (T_{gel} 25 °C to 30 °C). Small-angle neutron and X-ray scattering methods probed the arrested AHR microstructure to extract an effective interaction strength between rods on a reduced temperature scale, as defined by a dimensionless sticky parameter, τ_{eff}.

AHR suspensions exhibited qualitatively similar gel and glass transition behavior, but the boundaries were quantitatively shifted in L/D, φ, and T. On an absolute temperature scale, the critical gel-like boundary increased with L/D, while the critical glass volume fraction φ_g decreased significantly with L/D. However, on a reduced temperature scale, the measured gel boundary τ_{eff} appeared nearly independent of L/D for conditions below the hard rod glass line. This finding suggested an extended theory of corresponding states could also apply to anisotropic particle systems, as observed for similar short-range isotropic systems. These results prompted the mapping of a fundamental AHR state diagram in terms of the dimensionless variables L/D, φ, and τ_{eff} to compare various systems in literature. The AHR experiments showed good agreement with other mode-coupling simulations of hard rods and adhesive rods, which closely followed the predicted ideal glass boundaries. The proposed state diagram links the behavior of hard spheres, adhesive spheres, hard rods, and adhesive rods, providing a new way to conceptualize and map the intersecting boundaries between states that compete for fluidity, connectivity, rigidity, phase separation, and liquid crystal formation. The tunable AHR system and fundamental state diagram developed in this work can be used to define, guide, and predict the equilibrium and non-equilibrium state boundaries for other more complex molecules, polymers, anisotropic colloids, and proteins.