Slow dynamics of colloids in porous media: the roles of confinement and caging

J. Kurzidim and G. Kahl

Technische Universitat Wien, Institut fur Theoretische Physik and Center for Computational Materials Science, Wiedner Hauptstraße 8–10, 1160 Wien, Austria,
E–mail: kurzidim@cmt.tuwien.ac.at

Using molecular dynamics simulations, we have studied the dynamic arrest of a dense hard-sphere fluid moving in a disordered configuration of hard-sphere obstacles. The high density and the quenched disorder lead to two distinct dynamic arrest mechanisms-confinement and caging-that can also be observed for instance in the movement of proteins in cytoplasm. We have investigated the specific case of "quenched-annealed" systems in which the obstacles are quenched from an equilibrium fluid, and the fluid particles are subsequently inserted at arbitrary positions. Upon varying the two control parameters of the system (the volume fractions of the fluid and of the obstacles) we unveiled scenarios of both discontinuous and continuous dynamic arrest, anomalous diffusion, as well as a decoupling of the time scales for the relaxation of the single-particle and the collective correlators of the system. Our observations are consistent with many predictions by a recent extension of mode-coupling theory to systems with quenched disorder. In order to elucidate the microscopic origin of the observed dynamic arrest scenarios, we performed a Delaunay decomposition of the pore structure. We were thus able to distinguish between particles that are "free" (located in the void percolating through space) and "trapped" (confined in a void of finite volume). For these two classes of fluid particles we separately evaluated various dynamic correlators such as the single-particle intermediate scattering function, the mean-squared displacement and its logarithmic derivative, as well as the self part of the van Hove function. We thereby demonstrated that the free and the trapped particles exhibit nontrivial differences in their dynamic properties, which may serve as a basis for more refined theories.