Current Opinion in Colloid & Interface Science 12 (2007) 297–306

Current Opinion in
COLLOID and
INTERFACE SCIENCE

www.elsevier.com/locate/cocis

Dynamical fluctuation effects in glassy colloidal suspensions

Kenneth S. Schweizer *

Department of Materials Science and Frederick Seitz Materials Research Laboratory University of Illinois, Urbana, IL, 61801, USA

Received 28 July 2007; accepted 30 July 2007
Available online 9 August 2007

Abstract

Fundamental understanding of heterogeneous dynamics in concentrated glassy hard sphere fluids and colloidal suspensions, even at the single particle level, requires major theoretical advances. Recent simulations and confocal microscopy experiments suggest strong nongaussian dynamical fluctuation effects and activated transport emerge well before an apparent kinetic glass transition is reached. New theoretical approaches that can predict the observable signatures of intermittent large amplitude motions and the associated fluctuation phenomena are discussed. Comparisons are made with experiments, computer simulations, and prior theory for average dynamical properties.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Colloidal suspensions; Hard spheres; Glassy dynamics; Caging; Nongaussian fluctuations; Dynamic heterogeneity; Activated barrier hopping

1. Introduction

Hard sphere fluids have long served as the basic reference system for understanding the consequences of entropy and excluded volume in thermal liquids. Suspensions of hard sphere colloids are their real world surrogates and play an important role in modern colloid and materials science. The structure, equilibrium phase behavior, and dynamics of hard spheres in the normal fluid state (defined as volume fractions below the onset of crystallization, $\phi \sim 0.494$) are well understood [1]. A simple dynamical description of the latter built on binary collisions weakly perturbed by structural packing constraints ("caging") is largely adequate [2]. However, at higher volume fractions, which is the analog of the supercooled regime for thermal liquids, particle motions slow down dramatically, viscoelasticity emerges, and a disordered solid, a glass, forms on the experimental time scale [1,3••,4]. Ideal mode coupling theory (MCT) [3••,5••] is the first microscopic description of glassy hard sphere dynamics and describes well many "average" dynamical [3••,6•,7•] and mechanical [8] properties as probed by traditional ensemble-averaged methods. Recent advances in the imaging of colloidal suspensions based on confocal microscopy enables new "dynamical fluctuation" processes to be quantified, particularly at the single particle level where good statistical sampling can be achieved [9•]. The introduction of short range attractions results in novel dynamical arrest phenomena (gelation), and multiple aspects of the average consequences of physical bond formation at high volume fractions have been successfully predicted by ideal MCT [10•].

One might think the problem of glassy dynamics in quiescent hard sphere fluids and suspensions is solved. I believe this is not true for the reasons that form the subject of this article. Most fundamentally, a host of dynamical fluctuation phenomena that explicitly probe the nongaussian nature of particle motions, of widely recognized importance in supercooled thermal liquids [11], are not properly described by MCT. This article discusses recent theoretical attempts to treat such effects for hard spheres focused on the conceptually simplest *single particle* level, which is the aspect most well established in colloid experiments and fluid simulations. Such elementary dynamical fluctuation phenomena have received little quantitative theoretical analysis. Only approaches that can predict (or have the potential to) transport properties and time correlation functions, including the nongaussian aspects, are discussed. Determining the correctness of theories requires significant input from both simulation and experiment, and recent progress on these fronts is also summarized in an integrated manner.

Many aspects of the experimental phenomenology of supercooled liquids can be rationalized based on vastly different

* Tel.: +1 217 333 6440; fax: +1 217 333 2736.
E-mail address: kschweiz@uiuc.edu.

1359-0294/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cocis.2007.07.013

physical pictures. This thorny issue of "degeneracy of explanation" is potentially severe for suspensions composed of colloids of diameter $\sigma \sim 300$ nm–2 μm. The reason is that the Brownian time scale, defined as $\tau_0 \equiv \zeta\sigma^2/k_BT = \sigma^2/D_0$ (where D_0 is the dilute solution Stokes–Einstein diffusion constant), is typically 0.1–30 s, roughly 10–12 orders of magnitude larger the analogous time scale for atomic or molecular liquids. Since experiments generally measure dynamics only up to 100–10,000 s, the degree of slowing down beyond the normal dense fluid region is limited to a "glassy precursor" regime and quantitative aspects are necessarily important. For example, the shear viscosity increases by only a factor of ~ 100 as the volume fraction increases from 0.5 to the laboratory vitrification value of 0.57–0.58 [12•], which is far below random close packing (RCP) at $\phi_{RCP} \sim 0.64$. There also exist multiple real world complications, usually ignored in theoretical and/or simulation studies, which should be kept in mind. (1) Long range hydrodynamic interactions are the primary difference between hard sphere fluids and suspensions. Simulations that neglect them based on Newtonian, Brownian (no inertia or momentum conservation), stochastic, and even Monte Carlo dynamics all agree on the basic one and two body aspects of glassy precursor dynamics [13,14•,15–17•]. (2) Polydispersity renders difficult the accurate determination of volume fraction, increases ϕ_{RCP}, and accelerates dynamics. (3) Gravity and sedimentation modifies the kinetic vitrification process [18,19]. (4) Deviations from the hard sphere potential exist arising from grafted molecular layers, residual charge [9•] and/or particle deformability [20•]. (5) Physical aging can occur associated with intrinsic dynamical time scales exceeding laboratory measurement time scales [9•,19].

In Section 2 the concept of "average" versus "fluctuation" dynamical properties is discussed. Section 3 summarizes recent theoretical work, which is contrasted with computer simulations and experiments in Sections 4 and 5, respectively. The article concludes in Section 6 with a brief summary and future outlook.

2. Average and fluctuation dynamical properties and phenomena

Ensemble-averaged dynamical properties fall into two broad classes : scalars and time-dependent functions. Rheological properties, except for the viscosity, will not be discussed [8]. An average property is nonzero for a strictly gaussian dynamical process. Examples are the self-diffusion constant D, the shear viscosity η, the particle mean square displacement, $\mathrm{MSD}(t) \equiv \langle(\vec{r}(t) - \vec{r}(0))^2\rangle$, the single particle (incoherent) dynamic structure factor at a wavevector q, $F_s(q,t) \equiv \langle e^{i\vec{q}\bullet(\vec{r}(t)-\vec{r}(0))}\rangle$, and the normalized collective dynamic structure factor, $F(q,t) \equiv S(q,t)/S(q)$. The latter describes the time autocorrelation of total density fluctuations, $\delta\rho(q)$, on a length scale ~ $2\pi/q$, where $S(q)$ is the equilibrium structure factor. Length scale dependent relaxation times, $\tau_{inc}(q)$ and $\tau(q)$, can be defined from $F_s(q,t)$ and $F(q,t)$, respectively. The collective structural relaxation time is usually identified with the cage scale peak of $S(q)$ at $q = q^* \sim 2\pi/\sigma$ which quantifies short range order; its single particle analog, τ^*, is defined as $F_s(q^*, \tau^*) \equiv e^{-1}$. Fig. 1 indicates the qualitative behavior of some average properties: (i) the emergence of a q-dependent, 2-step decay at high volume fractions corresponding to a fast and local "in cage" β-process and a slow "cage escape" α-process [3••,4,5••], (ii) strong volume fraction dependence of scalars, and (iii) intermediate time anomalous (nonFickian) diffusion, $\mathrm{MSD}(t) \propto t^{\triangle(\phi)}$, characterized by the smallest, less than unity exponent, Δ [21•].

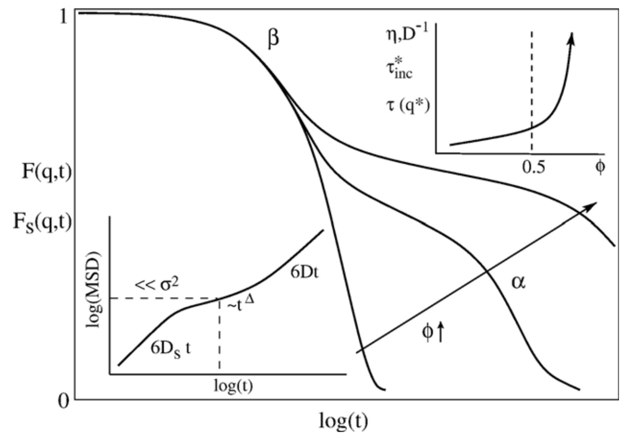

Fig. 1. Schematic of some average dynamical properties. The main panel shows the time-dependent dynamic structure factors for various volume fractions and cage scale wavevectors. A two-step decay, corresponding to a fast β and slow α process separated by a quasi-plateau, emerges at high volume fractions. The insets show: (i) log–log sketch of the time-dependent mean square displacement where the regime of maximally nonFickian diffusion is characterized by an effective exponent $\triangle$, and (ii) log-linear plot of the rapid growth of scalar properties (viscosity, inverse diffusion constant, collective and single particle alpha relaxation times) which change functional forms (and need not all be identical) as the normal fluid regime is exited.

Fluctuation properties are either exactly zero if the dynamics is a gaussian process or exhibit *qualitative* deviations from gaussian behavior. The relevant phenomena are schematically illustrated in Fig. 2 and include the following. (i) "Decoupling" of diffusive and relaxation processes as encoded in a volume fraction dependence of the product of the self-diffusion constant and shear viscosity, $D\eta$, or its purely single particle analog $D\tau^*$. Based on a gaussian or Stokes–Einstein perspective these "decoupling factors" should not depend on volume fraction. (ii) The traditional nongaussian parameter (NGP), $\alpha_2(t) \equiv \{3\langle r^4(t)\rangle/5\langle r^2(t)\rangle^2\} - 1$, is zero for a gaussian process and is a measure of dynamic heterogeneity on the late β/early α time scale when the MSD$<<\sigma^2$. Its maximum value and corresponding time scale grow in a distinctive manner with volume fraction. (iii) A recently proposed new NGP, defined as $\gamma_2(t) \equiv (1/3)\langle r^2(t)\rangle\langle 1/r^2(t)\rangle - 1$ [27••], preferentially weights deviations from gaussian dynamics on the slowest α -relaxation time scale. The asymmetric shape of this function, and the larger amplitude and much stronger volume fraction dependence of its characteristic time scale, contrast sharply with the more well studied NGP. (iv) For a Fickian process $F_s(q,t) \rightarrow e^{-q^2Dt}$. Nongaussian effects can be quantified at long times via a length-scale dependent diffusion constant as $F_s(q,t) \rightarrow e^{-q^2D(q)t}$, or relaxation time as $F_s(q,t) \equiv e^{-t/\tau(q)}$. A characteristic crossover length scale for attainment of Fickian diffusion, $\xi_D \propto 1/q_D$, corresponds to the

Download English Version:

https://daneshyari.com/en/article/603215

Download Persian Version:

https://daneshyari.com/article/603215

Daneshyari.com