Equilibration of Concentrated Hard Sphere Fluids

Gabriel Pérez-Ángel[1], Rigoberto Juárez-Maldonado[2,3], Alejandro Vizcarra-Rendón[3], Pedro E. Ramírez-González[2], Luis Enrique Sánchez-Díaz[2], and Magdaleno Medina-Noyola[2]

(1) Departamento de Física Aplicada CINVESTAV-IPN, Unidad Mérida Apartado Postal 73 Cordemex 97310. Mérida, Yuc., Mexico

(2) Instituto de Física "Manuel Sandoval Vallarta", Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, 78000 San Luis Potosí, SLP, México and

(3) Unidad Académica de Física, Universidad Autónoma de Zacatecas, Paseo la Bufa y Calzada Solidaridad, 98600, Zacatecas, Zac., Mexico

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We report a systematic molecular dynamics study of the isochoric equilibration of hard-sphere fluids in their metastable regime close to the glass transition. The thermalization process starts with the system prepared in a non-equilibrium state with the desired final volume fraction ϕ but with a prescribed *non-equilibrium* static structure factor $S_0(k;\phi)$. The evolution of the α-relaxation time $\tau_\alpha(k)$ and long-time self-diffusion coefficient D_L as a function of the evolution time t_w is then monitored for an array of volume fractions. For a given waiting time the plot of $\tau_\alpha(k;\phi,t_w)$ as a function of ϕ exhibits two regimes corresponding to samples that have fully equilibrated within this waiting time ($\phi \leq \phi^{(c)}(t_w)$), and to samples for which equilibration is not yet complete ($\phi \geq \phi^{(c)}(t_w)$). The crossover volume fraction $\phi^{(c)}(t_w)$ increases with t_w but seems to saturate to a value $\phi^{(a)} \equiv \phi^{(c)}(t_w \to \infty) \approx 0.582$. We also find that the waiting time $t_w^{eq}(\phi)$ required to equilibrate a system grows faster than the corresponding equilibrium relaxation time, $t_w^{eq}(\phi) \approx 0.27 \times [\tau_\alpha^{eq}(k;\phi)]^{1.43}$, and that both characteristic times increase strongly as ϕ approaches $\phi^{(a)}$, thus suggesting that the measurement of *equilibrium* properties at and above $\phi^{(a)}$ is experimentally impossible.

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Above a certain size polydispersity, real and simulated hard sphere liquids fail to crystalize for volume fractions ϕ beyond the freezing point $\phi^{(f)} = 0.494$ of the monodisperse system [1–8]. As ϕ increases the viscosity increases enormously, and the metastable liquid eventually becomes an amorphous solid. Mode coupling theory (MCT) [9, 10] predicts a transition from metastable fluid to ideal nonergodic states, characterized by the vanishing of the long-time self-diffusion coefficient D_L and the divergence of both, the α-relaxation time τ_α and the viscosity η. For the hard-sphere fluid the phenomenology predicted by MCT at $\phi^{(a)} \approx 0.52$ has been essentially confirmed by the experimental observations in hard-sphere colloidal suspensions at $\phi_{exp}^{(a)} \approx 0.58$ [11, 12], although a number of intrinsic experimental uncertainties render the precise determination of $\phi_{exp}^{(a)}$ a topic of recurrent scientific discussion [8, 11–15].

The recent work of Brambilla et al. [15], however, seems to put the very experimental relevance of the divergent scenario predicted by MCT under severe questioning. By fitting their dynamic light scattering data with the asymptotic expression $\tau_\alpha(\phi) \sim (\phi^{(a)} - \phi)^{-\gamma}$, traditionally associated with MCT, these authors determined $\phi^{(a)}$ to be $\phi^{(a)} = 0.590 \pm 0.005$. If the ideal MCT picture were to be observed in their experiments, the measured $\tau_\alpha(\phi)$ should be infinite for $\phi > \phi^{(a)}$. Instead, for the volume fraction range $\phi^{(a)} < \phi \lesssim 0.6$, they report large but finite relaxation times. The main claim of these authors is that these measurements involve macroscopic states in which the system, instead of falling out of equilibrium, remains ergodic and enters a new dynamical regime where τ_α increases with volume fraction according to a different functional form, namely, $\tau_\alpha(\phi) \sim \tau_\infty \exp[A(\phi_0 - \phi)^{-\delta}]$.

This interpretation of Brambilla et al. rests on the assumption that their measurements indeed involve fully equilibrated systems. An alternative possibility, however, is that this is actually an unrealistic assumption: if the *equilibrium* relaxation time $\tau_\alpha(\phi)$ indeed diverges as $\phi \to \phi^{(a)}$, the system might require a similarly divergent *equilibration* time $t_w^{eq}(\phi)$. The experimentalist would then need to wait a diverging waiting time to measure equilibrium properties, which is an experimental impossibility. Thus, an alternative interpretation of their experimental results is that for $\phi \gtrsim \phi^{(a)}$ their systems have not fully equilibrated, even though the on-going irreversible evolution of the system may simply be technically imperceptible or difficult to measure. Motivated by these considerations, this work is aimed at studying the *incomplete* equilibration of concentrated hard-sphere systems close to the glass transition by means of systematic computer simulations, in which some of the intrinsic uncertainties of the experimental samples will be absent.

The basic simulation experiment consists of monitoring the irreversible evolution of a hard-sphere system initially prepared at a non-equilibrium state characterized by a prescribed volume fraction ϕ and by a non-equilibrium static structure factor $S_0(k;\phi)$. The irreversible evolution to equilibrium is then described in

terms of the time-evolving non-equilibrium static structure factor $S_{t_w}(k;\phi)$ and self intermediate scattering function (Self-ISF) $F_S(k,\tau,t_w)$, where t_w is the evolution (or "waiting") time after the system was prepared. The long-t_w asymptotic limit of these properties is, of course, the *equilibrium* static structure factor $S^{eq}(k;\phi)$ and self-ISF $F_S^{eq}(k,\tau)$. Our interest is to determine the volume fractions for which equilibrium is reached within a given waiting time t_w.

We use event-driven molecular dynamics to simulate the evolution of $N = 1000$ particles in a volume V, with particle diameters σ evenly distributed between $\overline{\sigma}(1-w/2)$ and $\overline{\sigma}(1+w/2)$, with $\overline{\sigma}$ being the mean diameter. We consider the case $w = 0.3$, corresponding to a polydispersity $s_\sigma = w/\sqrt{12} = 0.0866$. According to the results reported in [3–5], at this polydispersity the system shows no evidence of crystallization for any volume fraction $\phi = (\pi/6)n\overline{\sigma^3}$, where $\overline{\sigma^3}$ is the third moment of the size distribution and n is the total number density $n \equiv N/V$. All the particles are assumed to have the same mass M. The length, mass, and time units employed are, respectively, $\overline{\sigma}$, M, and $\overline{\sigma}\sqrt{M/k_BT}$.

To produce the initial configurations we used soft-particle molecular dynamics to simulate the evolution of a set of initially overlapping, randomly placed particles, with the correct distribution of diameters, interacting through a short-ranged repulsive soft (but increasingly harder) interaction, and in the presence of strong dissipation. For ϕ below the random close packing limit, this system evolves rapidly into a disordered configuration with no overlaps. These non-thermalized hard-sphere configurations are then given random velocities generated by a Maxwell-Boltzmann distribution, with k_BT set as the energy unit. These configurations are then used as the starting configurations for the event-driven simulation of the HS equilibration process.

The simulations were carried for an array of values of ϕ between 0.480 and 0.595. For each such volume fraction we used waiting times from 1 to 10^5 in powers of 10. The sequence of configurations obtained is employed to generate the Self-ISF $F_S(k,\tau,t_w) \equiv (1/N)\langle\sum_{i=1}^{N}\exp\left[i\mathbf{k}\cdot(\mathbf{r}_i(t_w+\tau)-\mathbf{r}_i(t_w))\right]\rangle$ and the mean squared displacement (MSD) $\langle(\Delta\mathbf{r}(\tau;t_w))^2\rangle \equiv (1/N)\langle\sum_{i=1}^{N}[\mathbf{r}_i(t_w+\tau)-\mathbf{r}_i(t_w)]^2\rangle$, where $\mathbf{r}_i(t)$ is the position of the ith particle at time t, τ is the *correlation* time, and the brackets indicate averaging over (at least) 20 independent realizations. $F_S(k,\tau;t_w)$ is evaluated at $k = 7.1$, close to the main peak of $S^{eq}(k;\phi)$ for all the values of ϕ considered. The α-relaxation time $\tau_\alpha(k;\phi,t_w)$ is defined by the condition $F_S(k,\tau_\alpha,t_w) = 1/e$, and the long-time self-diffusion coefficient D_L by $D_L(\phi;t_w) \equiv \lim_{\tau\to\infty}\langle(\Delta\mathbf{r}(\tau;t_w))^2\rangle/6\tau$.

Let us illustrate the results of this procedure for one specific volume fraction, namely, $\phi = 0.575$. In Fig. 1(a) we present the simulation results for $F_S(k,\tau;t_w)$ evaluated at $k = 7.1$ as a function of the correlation time τ for the sequence of waiting times $t_w = 10^0,\ 10^1, ..., 10^5$. This sequence exhibits the increasing slowing down of the dynamics as the system approaches its equilibrium state and illustrates the fact that $F_S(k,\tau;t_w)$ saturates to its equilibrium value $F_S^{eq}(k,\tau)$ after a certain *equilibration waiting time* $t_w^{eq}(\phi)$. For example, from the illustrative data in the figure we find that $t_w^{eq}(\phi = 0.575) \approx 10^4$. A similar evolution and saturation is observed in the static structure factor $S_{t_w}(k;\phi)$, although the changes with t_w are not as dramatic as observed in $F_S(k,\tau;t_w)$; the inset of Fig. 1(a) presents the initial static structure factor $S_0(k;\phi) \equiv S_{t_w=0}(k;\phi)$ and the final equilibrium $S^{eq}(k;\phi)$. From the data for $F_S(k,\tau;t_w)$ in this figure we can determine the α-relaxation time $\tau_\alpha(k;\phi,t_w)$ as a function of t_w. The results indicate that the α-relaxation time $\tau_\alpha(k;\phi = 0.575,t_w)$ saturates approximately to its equilibrium value $\tau_\alpha^{eq}(k;\phi = 0.575) \approx 2\times10^2$ within the equilibration waiting time $t_w^{eq}(\phi = 0.575) \approx 10^4$.

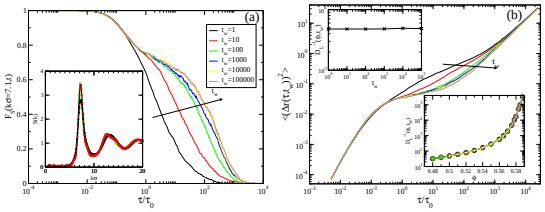

FIG. 1: (a) Self intermediate scattering function $F_S(k,\tau;t_w)$ evaluated at $k = 7.1$ and (b) mean squared displacement $\langle(\Delta\mathbf{r}(\tau;t_w))^2\rangle$ of a polydisperse hard-sphere system at volume fraction $\phi = 0.575$ and polydispersity $s = 0.0866$ as a function of the correlation time τ for waiting times $t_w = 10^0,\ 10^1, ..., 10^5$. The inset of (a) shows the corresponding $S_0(k;\phi)$ (black circles) and $S^{eq}(k;\phi)$ (red squares). The upper inset of (b) shows the inverse long-time self-diffusion coefficient, $D_L^{-1}(\phi;t_w)$, as a function of t_w for $\phi = 0.575$. The lower inset of (b) shows $D_L(\phi;t_w)$ as a function of ϕ at fixed waiting time, for $t_w = 10^0,\ 10^1, ..., 10^5$ (various overlapping symbols).

Fig. 1(b) presents the results for $\langle(\Delta\mathbf{r}(\tau;t_w))^2\rangle$ as a function of the correlation time τ for the illustrative volume fraction $\phi = 0.575$ and for the same sequence of waiting times. Contrary to the determination of $\tau_\alpha(k;\phi,t_w)$, which requires the evaluation of $F_S(k,\tau;t_w)$ within a rather local window of correlation times, the determination of $D_L(\phi;t_w)$ requires $\langle(\Delta\mathbf{r}(\tau;t_w))^2\rangle$ in a window of correlation times long enough to include the asymptotic diffusive regime where $\langle(\Delta\mathbf{r}(\tau;t_w))^2\rangle \approx 6D_L\tau$. This window must then be very long (of the order of 10^4 according to the data in the figure), even if the waiting time is small. As a consequence, the resulting value of $D_L(\phi;t_w)$ turns out to be rather insensitive to the value of t_w, as indicated in the upper-left inset of Fig. 1(b), which plots $D_L(\phi = 0.575;t_w)$ as a function of t_w. A similar behavior was observed in $D_L(\phi;t_w)$ at the other volume fractions,

and the results are presented in the lower inset of Fig. 1(b), which plots $D_L(\phi; t_w)$ as a function of ϕ for fixed waiting time $t_w = 10^0, 10^2, ..., 10^5$. The main feature to highlight is that the results for $D_L(\phi; t_w)$ are almost independent of t_w, and hence, $D_L(\phi; t_w)$ is not a reliable probe of the equilibration of the system compared with the t_w-dependence of $\tau_\alpha(k; \phi, t_w)$, that we now discuss.

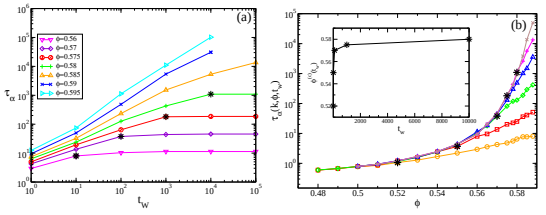

FIG. 2: Simulation data of the α-relaxation time $\tau_\alpha(k; \phi, t_w)$ of a polydisperse hard-sphere system ($s = 0.0866$) (a) as a function of t_w at fixed volume fraction and (b) as a function of volume fraction at fixed waiting time. The asterisks in (a) highlight the points $(t_w^{eq}(\phi), \tau_\alpha^{eq}(k; \phi))$, whereas the asterisks in (b) indicate the crossover volume fraction $\phi^{(c)}(t_w)$ at the various waiting times. The inset in (b) exhibits the evolution of $\phi^{(c)}(t_w)$ with waiting time.

Fig. 2(a) plots the dependence of the α-relaxation time $\tau_\alpha(k; \phi, t_w)$ as a function of waiting time t_w for fixed volume fraction ϕ. These plots confirm that beyond an equilibration waiting time $t_w^{eq}(\phi)$, the α-relaxation time $\tau_\alpha(k; \phi)$ saturates approximately to its equilibrium value $\tau_\alpha^{eq}(k; \phi)$. To emphasize these concepts we have highlighted the points $(t_w^{eq}(\phi), \tau_\alpha^{eq}(k; \phi))$ in the figure. In fact, we notice that the highlighted points $(t_w^{eq}(\phi), \tau_\alpha^{eq}(k; \phi))$ obey the approximate relation $t_w^{eq}(\phi) \approx 0.27 \times [\tau_\alpha^{eq}(k; \phi)]^{1.43}$, suggesting that the waiting time $t_w^{eq}(\phi)$ required to equilibrate a system is always longer than the corresponding equilibrium relaxation time $\tau_\alpha^{eq}(k; \phi)$, and that both characteristic times increase strongly with ϕ.

The same data for $\tau_\alpha(k; \phi, t_w)$ presented in Fig. 2(a) can also be displayed in a complementary manner, namely, plotting $\tau_\alpha(k; \phi, t_w)$ as a function of volume fraction for fixed waiting time t_w, and this is done in Fig. 2(b). The first feature to notice in each of the corresponding curves is that one can distinguish two regimes in volume fraction, namely, the low-ϕ (equilibrated) regime and the high-ϕ (non-equilibrated) regime, separated by a crossover volume fraction $\phi^{(c)}(t_w)$. Focusing, for example, on the results corresponding to $t_w = 10^3$, we notice that $\phi^{(c)}(t_w = 10^3) \approx 0.57$. In Fig. 2(b) we have highlighted the crossover points $(\phi^{(c)}(t_w), \tau_\alpha^{eq}(k; \phi))$. We observe that the resulting crossover volume fraction $\phi^{(c)}(t_w)$ first increases rather fast with t_w, but then slows down considerably, suggesting a saturation to a value slightly larger than 0.58, as indicated in the inset of Fig. 2(b).

One of the main products of the simulation results just presented is the determination of the volume fraction dependence of the *equilibrium* α-relaxation time $\tau_\alpha^{eq}(k; \phi)$. Clearly, our simulation experiment can determine this property only within the window $0 \leq \phi \leq \phi^{(c)}(t_w^{max})$, where t_w^{max} is the maximum waiting time achieved in the simulation experiment. In our case $t_w^{max} = 10^5$, yielding $\phi^{(c)}(t_w^{max}) \approx 0.58$. These results are plotted in Fig. 3(a) as solid circles. For $\phi \geq 0.58$ the t_w-dependent α-relaxation time $\tau_\alpha(k; \phi, t_w)$ did not saturate to its equilibrium value within the total duration of the present simulation experiment. These results are also plotted in Fig. 3(a) as empty circles, to denote insufficient equilibration. Thus, only the data in solid symbols are meaningful when comparing with the predictions of *equilibrium* theories such as MCT or the more recently developed self-consistent generalized Langevin equation (SCGLE) theory [16, 17]. In Fig. 3(a) we show, for example, a one-parameter fit of the equilibrium data ($\phi \leq 0.58$) obtained with the *full numerical solution* of the SCGLE theory (Ecs. (1), (2), and (5-8) of Ref [17] with $D^0 = \sqrt{\pi}/16\phi$, and with $k_c = 8.4823$ adjusted to fit these equilibrium data). According to this fit, $\tau_\alpha^{eq}(k; \phi)$ diverges at $\phi^{(a)} \approx 0.582$.

There is, of course, no reason to attempt to fit the volume fraction dependence of the whole set of (equilibrated and non-equilibrated) data in Fig. 3(a) in this manner. As a mere fitting exercise, however, we notice that these data can be fitted by the expression $\tau_\alpha(\phi) = \tau_\infty \exp[A(\phi_0 - \phi)^{-\delta}]$, thus finding $A = 0.02$, $\delta = 1.921$, $\tau_\infty = 0.21$ and $\phi_0 = 0.6235$ (dashed line in the figure). These values are rather similar to those that fit the experimental data of Brambilla et al. [15]. Another manner to see that the full set of data corresponding to $t_w = 10^5$ follows this ϕ-dependence is shown in the inset of Fig. 3(a), where we plot the logarithm of $[\tau_\alpha(k; \phi, t_w)/\tau_\infty]$ vs. $[A(\phi_0 - \phi)^{-\delta}]$. We find that within the resolution of the figure, these data do follow approximately this functional form in the metastable regime of volume fractions both before and beyond the crossover volume fraction $\phi^{(c)}(t_w = 10^5) \approx 0.58$ (pointed by an arrow). Amazingly enough, we find a similar behavior also for the shorter waiting times $t_w = 10^4$ and 10^3 using the same values for the parameters δ, C, and τ_∞ as for $t_w = 10^5$, but with $\phi_0 = 0.635$ and 0.631, respectively. In fact, in the inset of Fig. 3(a) we have also included the experimental data of Brambilla et al. [15] for $\phi > 0.5$, using the same parameters as above but with $\phi_0 = 0.637$. In reality we previously multiplied their experimental data of $\tau_\alpha(\phi)$ by the expression $D_S/D_0 = (1 - \phi)/(1 + 1.5\phi)$ for the short-time self-diffusion coefficient of the hard-sphere suspension (scaled with its zero-ϕ value D_0, [20]), as a simple manner to "substract" the effects of hydrodynamic interactions from their experimental data, so as to compare with our simulation results. This comparison suggests a completely similar phenomenology. In the present case, however, it is quite clear that the departure

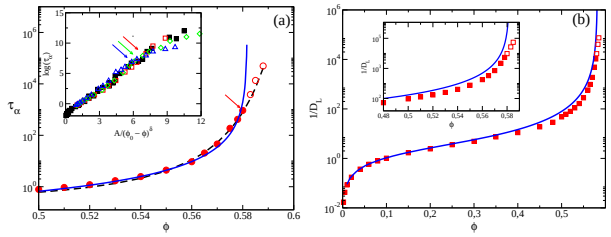

FIG. 3: Volume fraction dependence of (a) the α-relaxation time $\tau_\alpha(k;\phi,t_w = 10^5)$ and (b) the long-time self-diffusion coefficient $D_L(\phi;t_w = 10^5)$ of the polydisperse HS system. The solid (empty) symbols denote simulation data of fully equilibrated (insufficiently equilibrated) systems. The solid lines are the predictions of the SCGLE theory. The dashed line in (a) corresponds to $\tau_\alpha(\phi) = \tau_\infty \exp[A(\phi_0-\phi)^{-\delta}]$ with $A = 0.02$ and $\delta = 1.9212$, $\tau_\infty = 0.21$, and $\phi_0 = 0.6235$. The inset in (a) plots $\tau_\alpha(k;\phi,t_w)$ for $t_w = 10^5$ (circles), 10^4 (squares) and 10^3 (triangles) using the same values for δ, C, and τ_∞ but with $\phi_0 = 0.635$ and 0.631, and 0.630 for $t_w = 10^3$ and 10^4, and 10^5, respectively. The inset of (b) is a zoom of the metastable regime of the main figure.

of $\tau_\alpha(k;\phi,t_w = 10^5)$ from the equilibrium curve predicted by the SCGLE theory near $\phi^{(a)}$ is due to the insufficient equilibration of the system within the maximum waiting time $t_w^{max} = 10^5$ of our simulation, and this suggest that a similar situation might hold in the experiments reported by Brambilla et al. [15].

Let us finally mention that a similar scenario is observed in the results for $D_L(\phi;t_w)$. Thus, in Fig. 3(b) we plot the simulation results for $D_L(\phi;t_w = 10^5)$ with the empty symbols indicating again insufficient equilibration. The solid line of Fig. 3(b) is the *prediction* of the SCGLE theory with the value $k_c = 8.4823$ kept from the fit of the data for $\tau_\alpha(k;\phi,t_w = 10^5)$ in 3(a). Despite the small quantitative disagreements with the simulation data, amplified in the inset of 3(b), the SCGLE fit provides a remarkably good overall description of the volume fraction dependence of the equilibrium results for $D_L(\phi;t_w = 10^5)$.

The results just presented suggest that any simulation aimed at determining the *equilibrium* value of dynamic order parameters such as $\tau_\alpha(k;\phi,t_w)$ and $D_L(\phi;t_w)$ near the dynamic arrest transition is bound to be limited by the duration of the simulation experiment, represented by the maximum waiting time t_w involved. This limits the determination of these equilibrium values to the window of volume fractions $0 \le \phi \le \phi^{(c)}(t_w^{max})$. For $\phi \ge \phi^{(c)}(t_w^{max})$, the simulation results will be reporting the properties of an insufficiently equilibrated system. The results presented here indicate that if we want to enlarge this window we would have to go to exponentially longer waiting times, which is bound sooner or later become a lost battle. There is, of course, no obvious reason to believe that a different situation will prevail in experimental samples. In the meanwhile,it is clear that the correct analysis of the data corresponding to incompletely equilibrated conditions must be made in the framework of a non-equilibrium theory. In fact, one of the motivations to carry out the present simulation experiments was the need to count with reliable data aimed at explicitly exhibiting the main features of incompletely equilibrated systems that will serve as a reference to test the recently-developed non-equilibrium extension of the SCGLE theory [21]. This analysis is already in progress, and the preliminary results seem highly encouraging.

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