RAPID COMMUNICATIONS

PHYSICAL REVIEW E **96**, 020602(R) (2017)

Brownian versus Newtonian devitrification of hard-sphere glasses

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(Received 11 July 2017; published 23 August 2017)

In a recent molecular dynamics simulation work it has been shown that glasses composed of hard spheres crystallize via cooperative, stochastic particle displacements called avalanches [E. Sanz *et al.*, Proc. Natl. Acad. Sci. USA **111**, 75 (2014)]. In this Rapid Communication we investigate if such a devitrification mechanism is also present when the dynamics is Brownian rather than Newtonian. The research is motivated in part by the fact that colloidal suspensions, an experimental realization of hard-sphere systems, undergo Brownian motion. We find that Brownian hard-sphere glasses do crystallize via avalanches with very similar characteristics to those found in the Newtonian case. We briefly discuss the implications of these findings for experiments on colloids.

DOI: 10.1103/PhysRevE.96.020602

I. INTRODUCTION

Crystallization of glasses, also known as devitrification [1–3], is an undesirable process since it can lead to dramatic changes in the physical properties of the material. The simplest system that shows a glass-crystal transition is probably that composed of hard spheres. From recent molecular dynamics simulations it has been concluded that hard-sphere glasses crystallize gradually without the need for particle diffusion [4], not even within the regions where crystals appear and grow [5]. Crystallites appear and grow in a steplike fashion, as a consequence of the development of stochastic collective particle displacements (avalanches) that punctuate quiescent periods [6]. These avalanches induce the appearance and growth of crystallites in nearby regions of the glass [6].

The avalanches that mediate devitrification resemble spatially heterogeneous dynamics, in the form of stringlike clusters of cooperatively jumping particles, that have been observed below and above the glass transition in either two and three dimensions [7] in a broad variety of glass formers [8–15], including supercooled liquids [16–22], supercooled water [23,24], metallic glasses [25,26], and hard-sphere and colloidal glasses [27–29].

The simulation work [6] where the avalanche-mediated devitrification pathway was proposed left open questions regarding the possibility of observing such a mechanism in experiments on colloids. One such question is the role of dynamics. These were Newtonian in the simulations of Ref. [6] whereas colloidal suspensions follow Brownian dynamics (BD). Therefore, in this work we perform Brownian dynamics simulations of hard-sphere glasses and compare the devitrification mechanism with that previously observed with Newtonian dynamics [6]. We find that the mechanism is basically the same in both cases, supporting the idea that colloidal glasses may devitrify via avalanches, a point explored further in Sec. IV.

II. SIMULATION DETAILS

We perform simulations with $N = 3200$ particles of diameter σ at constant volume V (cubic box under periodic boundary conditions) for densities above the glass-transition volume fraction $\phi_g = 0.585$ [4,30] (being $\phi = \frac{\pi}{6}N\sigma^3/V$). In particular, we simulate at packing fractions 0.610 and 0.613. In order to avoid the formation of crystallites in the preparation of the initial configuration for our simulations (a glass of monodisperse spheres), we use the constrained aging protocol described in Ref. [31].

In order to be able to efficiently simulate hard spheres (HSs) in molecular dynamics (MD), Jover and co-workers have recently proposed a pseudo-hard-sphere (PHS) interaction potential [32] that recovers results expected for HS not only in equilibrium [30,32] but also out of equilibrium [30]. In the latter case, we have recently demonstrated that by simulating via MD a dense monodisperse PHS suspension, not only the location of the glass transition ϕ_g, but also the devitrification mechanism [30] coincides with the one observed in monodisperse HS glasses [6]. The appearance of stochastic avalanches is responsible for an increase of the crystallinity; the only (minor) difference is that PHS glasses crystallize earlier than HS ones for a given density, due to the fact that the development of avalanches is eased in the PHS glass by a small degree of overlapping between particles enabled by the potential softness [30].

Throughout our study, we will consider particles interacting via the PHS potential [32], i.e., a cut-and-shifted Mie potential with exponents (50, 49),

$$\Phi_{50,49}(r)\begin{cases}50\left(\frac{50}{49}\right)^{49}\epsilon\left[\left(\frac{\sigma}{r}\right)^{50}-\left(\frac{\sigma}{r}\right)^{49}\right]+\epsilon, & r<\left(\frac{50}{49}\right)\sigma,\\ 0, & r\geqslant\left(\frac{50}{49}\right)\sigma,\end{cases} \tag{1}$$

where r is the interparticle distance. In order for the potential above to mimic hard spheres, one must set $\epsilon = k_BT/1.5$ [32].

We use the GROMACS package [33] to perform MD simulations of this potential with the argon parameters $\sigma = 3.405$ Å, $\epsilon/k_B = 119.87$ K, $m = 6.64\times10^{-26}$ kg. The simulation temperature is therefore $T = 1.5\epsilon/k_B = 179.71$ K. We use $\tau = [\sigma\sqrt{m/(k_BT)}]$ to reduce time: $t_N = t/\tau$ (in one reduced time unit, a free particle would move a distance of about one diameter). In the remainder of this Rapid Communication we refer to t_N as Newtonian time. We integrate the equations of motion with a leapfrog algorithm [34] with a time step of $5.68\times10^{-4}t_N$ (1.0 fs). Temperature is kept constant using the

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v-rescale thermostat [35] with a relaxation time of $0.568 t_N$ (1.0 ps) [36].

For Brownian dynamics we use a bespoke Monte Carlo (MC) code. Following Ref. [37], we can convert MC cycles (a cycle consists of a trial move per particle) t_{MC} to Brownian time t_B through

$$t_B = \frac{a\delta^2 t_{\mathrm{MC}}}{6\sigma^2}, \tag{2}$$

where δ is the maximum particle displacement (fixed throughout the run), and a is the average acceptance of trial displacements. The dimensionless Brownian time is real time divided by the time it takes for a particle to diffuse its own diameter at infinite dilution, σ^2/D_0, where D_0 is the self-diffusion coefficient given by the Stokes-Einstein relation $D_0 = (k_B T)/(3\pi\eta\sigma)$, where η is the viscosity of the solvent. According to Ref. [37], in order for Eq. (2) to work, a must be at least 0.7. We have tuned δ for each simulated density so that a is 0.7. The values of δ used were $\delta_{0.610}/\sigma = 0.0102$ and $\delta_{0.613}/\sigma = 0.0098$, for volume fractions 0.610 and 0.613, respectively.

Following Ref. [6], we identify avalanche particles as those whose displacement during a given time interval (Δt) is larger than $\sigma/3$. The time interval Δt is set to one fifth of the duration of the crystallinity jump, both in MD and BD. Such a duration is identified as the time difference between crystallinity plateaus. Any Δt value comparable to such a duration would have given a qualitatively similar picture to that described below. The fraction of avalanche particles is then given by the number of avalanche particles N_{av} divided by N.

To evaluate the overall crystallinity of the system (X), we determine the total number of solidlike particles (N_{sol}) divided by N. Solidlike particles are established using a rotationally invariant local bond order parameter d_6 . As in Refs. [30,38], we first compute the number of neighbors $N_b(i)$ of each particle i using the parameter-free solid-angle-based nearest-neighbor (SANN) algorithm [39]; next, we compute the d_6 rotationally invariant order parameter for each pair of neighboring particles [see Eq. (3), where $m \in [-6,6]$ and Y_{6m} are the sixth-order spherical harmonics, and Eq. (4), where j represents each of the N_b neighbors of particle i],

$$q_{6m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{6m}(\theta_{ij},\phi_{ij}) \Bigg/ \left(\sum_{m=-6}^{6} q_{6m}(i) \cdot q_{6m}^*(i) \right)^{1/2}, \tag{3}$$

$$d_6(i,j) = \sum_{m=-6}^{6} q_{6m}(i) \cdot q_{6m}^*(j). \tag{4}$$

If the value of d_6 is greater than 0.7, two neighboring particles share a "solid connection." A particle is labeled as solidlike only when it shares at least six solid connections.

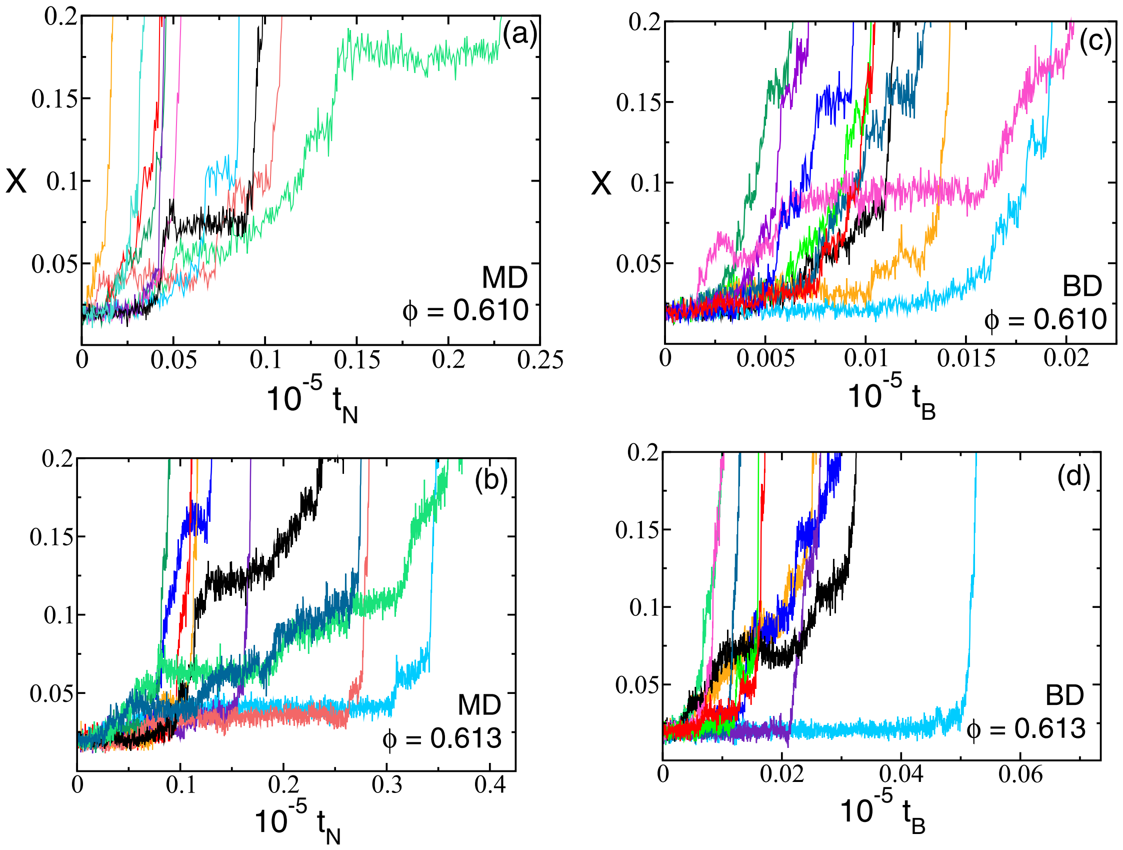

FIG. 1. X vs time for ten independent trajectories for MD (left column) and BD (right column) at $\phi = 0.610$ [(a) and (c)] and 0.613 [(b) and (d)], as indicated in the figures. Six of the runs at 0.610 are from Ref. [30].

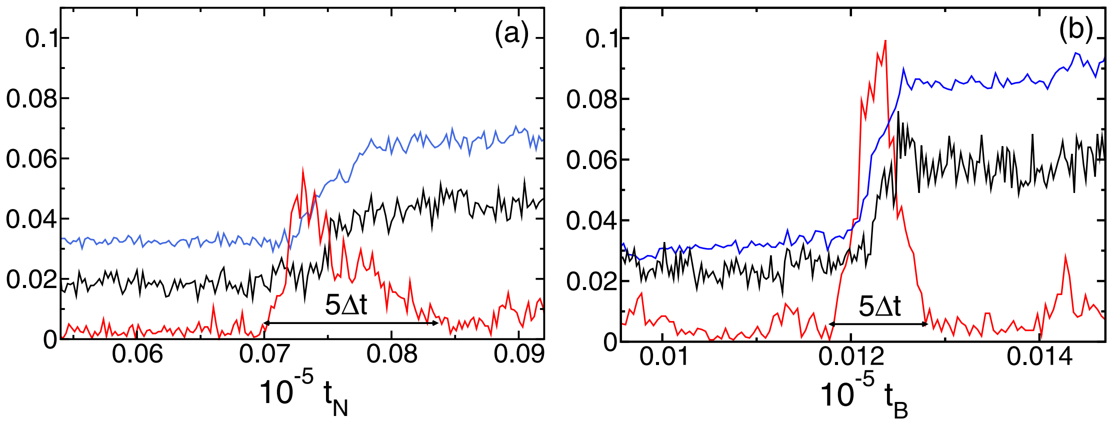

FIG. 2. MSD/σ^2 (in blue, top line), X (in black, middle curve), and N_{av}/N (in red, bottom curve) vs time for (a) an MD trajectory and (b) a BD one, each at $\phi = 0.613$.

III. RESULTS

To check if avalanches are seen in BD simulations, we launch both in MD and in BD ten independent trajectories starting from the same initial glassy configuration, each differing in the initial velocities (MD) or in the seed for the random number generator (BD). In Fig. 1 we show that in both sorts of dynamics (MD left and BD right columns) and for both studied packing fractions ($\phi = 0.610$ top and $\phi = 0.613$ bottom) the crystallinity increases in a steplike fashion, which is a clear signature of an avalanche-mediated mechanism of glass crystallization [6]. Once the crystallinity reaches a certain value (typically 7%–10%) the system crystallizes catastrophically and, eventually, X reaches nearly 1 in all trajectories (not shown in the scale of the figure). The fact that different trajectories starting from the same glassy configuration follow different crystallization paths underlines the stochastic nature of the avalanches [6,30]. In both BD and MD the avalanches become sharper and quiescent plateaus flatter and longer as the packing fraction increases, in agreement with previous observations for MD [30].

We now focus on a single crystallinity jump for $\phi = 0.613$ and analyze it comparing BD and MD. Figure 2 shows the mean square displacement MSD/σ^2, crystallinity X, and the fraction of avalanche particles N_{av}/N, for both an MD [Fig. 2(a)] and a BD [Fig. 2(b)] jump. In both cases, a sudden burst of N_{av}/N, corresponding to a steplike increase of MSD/σ^2, is followed by an increase of X. We conclude from this figure that crystallinity jumps are indeed caused by the appearance of avalanches for BD as well as for MD. For this particular example the population of avalanche particles, shown in red in Fig. 2, is about twice as large in the Brownian case. Such an avalanche causes a crystallinity jump also about twice as large (X increases by about 4% in BD versus nearly 2% in MD). Avalanches are not always larger in Brownian dynamics. In fact, on average, the crystallinity jumps for a given packing fraction are of the same magnitude for both sorts of dynamics [see Fig. 3(a)].

We have also examined whether the nature of the displacements found during an avalanche is the same in both types of dynamics. In Newtonian dynamics it has been reported that particles move cooperatively [6]. This is illustrated in Fig. 4(a), where it is shown how avalanche particles follow long strings in MD. This feature can also be clearly seen in Fig. 4(b), corresponding to Brownian dynamics.

Our results suggest that avalanches develop due to a successful sequence of particle displacements, without any involvement of inertia in their development. Therefore, we conclude that the mechanism of devitrification is the same regardless of the microscopic dynamics of the system.

Having established the qualitative similarity of devitrification in both sorts of dynamics, we also seek to perform a more quantitative comparison. A quantitative aspect already

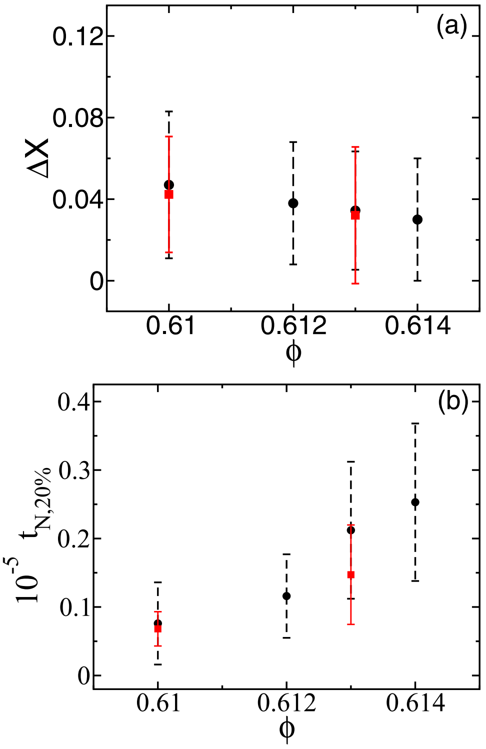

FIG. 3. (a) Mean crystallinity jump X at different ϕ for MD (black circles) and BD (red squares); (b) time needed to crystallize 20% of the system as a function of ϕ. 60% of data at 0.610 and all data at 0.612 and 0.614 are from Ref. [30].

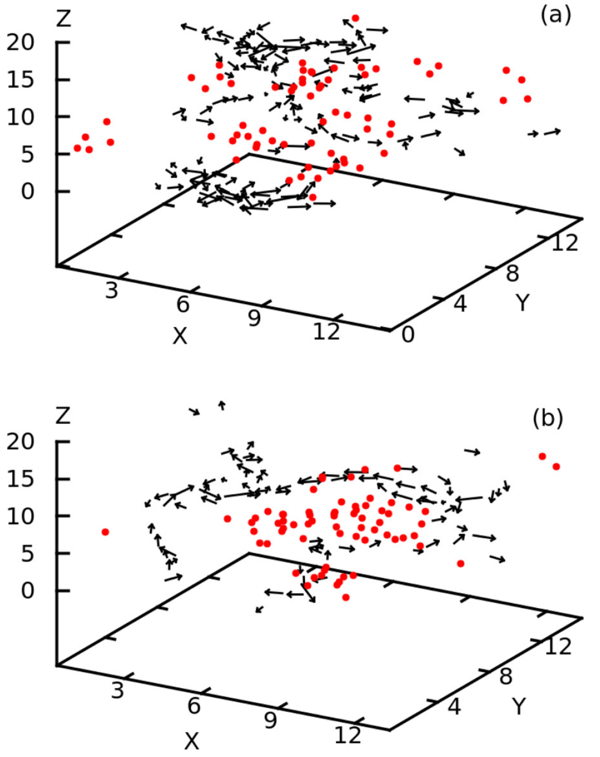

FIG. 4. Black arrows: Displacement vectors of avalanche particles represented in xyz. Red dots: Solidlike particles. (a) MD, (b) BD. Both at $\phi = 0.613$.

discussed above is the fact that the crystallinity jumps ΔX are on average of the same magnitude [Fig. 3(a)]. We are also interested in assessing whether avalanches occur, on average, at the same time. To do that we need a factor to convert t_B to t_N. There is in principle no physical way to get such a conversion factor *a priori*. However, we can empirically check if there is a proportionality between both times when a physically relevant process of the system takes place. We choose the diffusion of one particle over its diameter (MSD $= \sigma^2$) as such a process. Taking MSD $= \sigma^2$ defines t_B^σ and t_N^σ Brownian and Newtonian diffusive times, respectively. In Fig. 5 we plot t_N^σ / t_B^σ vs ϕ and find that the ratio follows a straight line. Of course, these calculations were performed for $\phi < \phi_g$, where there is diffusion. By extrapolating beyond the glass transition we get a ratio of 5.66 at the densities where we perform the study of glass devitrification (green dots in the figure). Therefore, we use $t_N = 5.66 t_B$ to convert from Brownian to Newtonian time.

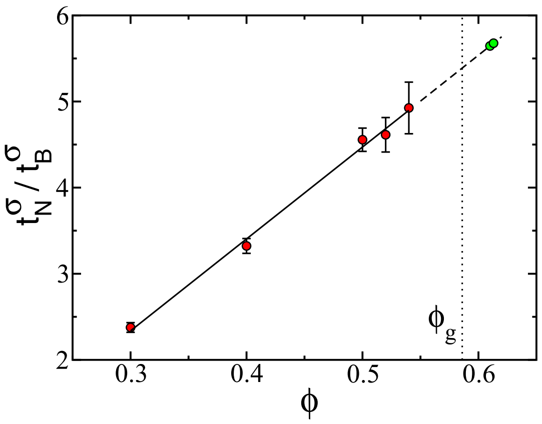

FIG. 5. Ratio between the Newtonian and the Brownian times required for a particle to diffuse its own diameter (MSD $= \sigma^2$) as a function of packing fraction. Red circles: Our calculations for $\phi < \phi_g$ ($\phi_g = 0.586$ [30]). Solid line: Linear fit to the red circles. Dashed line: Linear extrapolation to the packing fractions where we have studied devitrification (green circles). Error bars have been computed performing ten independent runs.

Computing the average crystallization time, defined as the average time required to reach $X =$ 20%, $t_{20\%}$, as a function of ϕ, we observe that both dynamics give the same $t_{20\%}$ after converting t_B to t_N, as explained above [Fig. 3(b)]. Therefore, by mapping Newtonian and Brownian times through a physical process below ϕ_g (diffusion of one diameter), we get a good mapping for another process above ϕ_g (devitrification).

IV. DISCUSSION

We have shown that the avalanche-mediated devitrification mechanism proposed for hard-sphere glasses with Newtonian dynamics [6] also holds when the dynamics are Brownian. We have further shown that processes described by the two kinds of dynamics can be quantitatively mapped onto one another. This suggests that the dynamics is only different before particles collide; processes that involve multiple collisions, such as diffusion in metastable fluids or devitrification, show the same behavior both qualitatively and quantitatively. Thus it is particle displacements rather than their velocities that are important. Introducing a new set of random velocities in a molecular dynamics simulation simply induces a new set of random displacements (velocities integrated over time), in much the same way that using a new seed for the random number generator in Brownian dynamics leads to different random displacements.

An immediate consequence of these findings is that colloidal glasses, which follow Brownian dynamics, should exhibit the same kind of avalanche-induced devitrification process as molecular and metallic glasses. Although there have been several experimental studies of dynamic heterogeneities in metastable colloidal fluids approaching the glass transition [27,28], fewer such investigations of the glass itself have been reported. An early experiment [27] using scanning confocal microscopy observed mainly small local rearrangements in a colloidal glass and did not find the more extensive avalanches that we report. One difficulty with searching for rare events with microscopy is that a huge amount of data must be stored and analyzed. On the other hand, a more recent experiment [40] using x-ray photon correlation spectroscopy found clear evidence of intermittent dynamics, which the authors attributed to avalanches, in hard-sphere colloidal glasses. Further studies would clearly be valuable. It would, for example, be interesting to vary the size of the scattering volume in a light or x-ray scattering experiment. With a relatively small number of particles in the volume, one should see, as in the simulations, clear intermittency with long quiescent periods. However, with a larger volume containing many particles, so that several avalanches occur simultaneously in different regions of the system, the dynamics would appear much more homogeneous (see, e.g., Supplemental Material for Ref. [6]). In this way, the size, frequency, and distribution of the avalanches could be elucidated.

Possible circumstantial experimental evidence for avalanches in colloidal systems comes from the observation that the nature of the crystallization process changes dramatically as the glass-transition concentration is crossed [38,41–43]. With increasing concentration, crystallization in metastable colloidal fluids becomes increasingly easy, resulting in small compact crystallites whose size decreases with concentration and may even tend to zero at the glass-transition concentration itself [44]. However, in the glass, devitrification leads to much larger irregularly shaped crystallites, suggesting that they might well be the result of the avalanches that we have found in simulations.

Finally, we remark that, although Brownian dynamics gives a more realistic description of colloidal systems than molecular dynamics, the algorithm that we have used here still neglects hydrodynamic interactions, the forces between particles transmitted by motion-induced flows in the suspending liquid. It seems likely that, as with dynamics in the metastable fluids below the glass transition [45], hydrodynamic interactions will affect the details, particularly the time scales, but will not alter the underlying picture.

Recently, we became aware of a paper by Yanagishima *et al.* [46]. These authors study by Brownian dynamics a system with softer interactions and find much the same avalanche phenomenology as we do for hard spheres in this and our earlier paper [6]. They further make a connection between devitrification and the aging process observed in noncrystallizing systems, and suggest that the avalanches involve collapsing force chains.

ACKNOWLEDGMENTS

C.V. and E.S. acknowledge the National Projects (Mineco) FIS2013-43209-P, FIS2016-78117-P, and FIS2016-78847-P, and a Ramon y Cajal tenure track. P.R.S. acknowledges the fellowship granted by the Universidad Complutense de Madrid for financial support.

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