Effect of Hydrodynamic Interactions on Self-Diffusion of Quasi-Two-Dimensional Colloidal Hard Spheres

Alice L. Thorneywork,[1] Roberto E. Rozas,[2,3] Roel P. A. Dullens,[1,*] and Jürgen Horbach[2,†]
[1]Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Park Road, Oxford OX1 3QZ, United Kingdom
[2]Institut für Theoretische Physik II: Soft Matter, Heinrich Heine-Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany
[3]Departamento de Física, Universidad del Bío-Bío, Collao 1202, Casilla 5C, Concepción, Chile

(Received 17 November 2014; revised manuscript received 1 July 2015; published 23 December 2015)

We compare experimental results from a quasi-two-dimensional colloidal hard sphere fluid to a Monte Carlo simulation of hard disks with small particle displacements. The experimental short-time self-diffusion coefficient D_S scaled by the diffusion coefficient at infinite dilution, D_0, strongly depends on the area fraction, pointing to significant hydrodynamic interactions at short times in the experiment, which are absent in the simulation. In contrast, the area fraction dependence of the experimental long-time self-diffusion coefficient D_L/D_0 is in quantitative agreement with D_L/D_0 obtained from the simulation. This indicates that the reduction in the particle mobility at short times due to hydrodynamic interactions does not lead to a proportional reduction in the long-time self-diffusion coefficient. Furthermore, the quantitative agreement between experiment and simulation at long times indicates that hydrodynamic interactions effectively do not affect the dependence of D_L/D_0 on the area fraction. In light of this, we discuss the link between structure and long-time self-diffusion in terms of a configurational excess entropy and do not find a simple exponential relation between these quantities for all fluid area fractions.

DOI: 10.1103/PhysRevLett.115.268301 PACS numbers: 82.70.Dd, 05.40.−a, 61.20.−p, 66.10.−x

Introduction.—Understanding the relationship between structure and dynamics is a long-standing problem in the study of fluids and glasses [1,2]. Many such links have been proposed, including a simple scaling relation between the diffusion coefficient and the excess entropy, via the radial distribution function [3–13]. Key in experimentally testing such a relation is the careful characterization of both the structure and dynamics of the system. For atomic liquids, while structural properties are readily available using scattering methods [14], the self-diffusion coefficients are usually only available for certain atomic species and a small range of temperatures [15–17]. Experimentally, colloidal suspensions are well-established model systems as both structural and dynamic information can be obtained in one experiment at a single particle level over a wide range of time scales using optical microscopy [18–32]. However, in addition to the direct interactions between particles, colloidal systems exhibit solvent-mediated hydrodynamic interactions (HI), not found in atomic systems. These often complicate or obscure direct relations between structural and dynamic properties, and thus, a detailed understanding of HI in colloidal model fluids is imperative for the interpretation of experimental results.

Disentangling the effects of direct and hydrodynamic interactions is an extremely complex problem, yet a crucial one in establishing a satisfactory relationship between the structure and dynamics of fluids. While it is well accepted that HI are important at short times [26,30,33–35], there is currently no consensus about the effect of HI at long times [23,28,36–40]. As a result, many theoretical and simulation studies of long-time dynamics either ignore the effect of HI altogether [41,42] or include them in an approximate manner, for example, using the effect of HI at short times [43,44]. It is therefore very difficult to determine whether deviations between experiment and theory originate from errors in the description of the direct interactions or whether they are due to the effects of HI.

In this Letter, we compare an experimental quasi-two-dimensional (2D) colloidal hard sphere fluid to a Monte Carlo (MC) simulation of hard disks with small particle displacement moves. In particular, we study the scaled short- and long-time self-diffusion coefficients, $D_{\mathrm{S,L}}/D_0$, with D_0 the diffusion coefficient at infinite dilution. While the scaled short-time self-diffusion coefficient of the experiment, D_S/D_0, strongly depends on the area fraction, pointing to significant HI at short times, quantitative agreement between experiment (with HI) and simulation (without HI) is found with respect to D_{L}/D_0. This directly indicates that the reduced particle mobility at short times, which results from hydrodynamic interactions, is not reflected in the long-time self-diffusion of the particles. In fact, the quantitative agreement between experiment and simulation with respect to D_L/D_0 implies that HI effectively do not affect the dependence of D_{L}/D_0 on the area fraction. Finally, as our experimental system is an excellent model for hard disks both structurally and dynamically at long times, we probe the proposed link between D_L/D_0 and the fluid structure in terms of the configurational excess entropy, S_2 [3,4]. As opposed to Ref. [5], we do not find a simple exponential relation between D_L/D_0 and S_2 for all fluid area fractions.

Experiment.—The quasi-2D colloidal system, as introduced in Ref. [22], consists of carboxylic acid functionalized melamine formaldehyde particles (Microparticles GmbH), with hard sphere diameters of $\sigma = 2.79\ \mu$m or 4.04 μm, dispersed in a 20/80 v/v% ethanol/water mixture. A wide range of area fractions, $\phi = 0.02$–0.65, within the fluid phase are studied. The particles sediment onto the base of a glass sample cell with a height of 200 μm, and as their gravitational lengths are 0.07 μm and 0.02 μm for the small and large particles, respectively, the out-of-plane fluctuations are negligible relative to the particle diameter [22]. The colloidal system is imaged using video microscopy and the particle positions acquired using standard particle tracking software [45].

Simulation.—MC simulations are equivalent to Brownian dynamics (BD) simulations provided that the maximal displacement Δ for the trial moves is infinitesimally small [46]. Recently, it has also been shown that for finite values of Δ a perfect matching between MC simulations and BD can be achieved if one rescales the MC time by the acceptance probability of the trial moves [47]. Here, we follow this protocol and, given the 2D nature of the experiment, perform MC simulations for systems of $N = 900$ hard disks in a square box with periodic boundary conditions, choosing the trial displacement for a single particle randomly from the interval $[-0.01\sigma, 0.01\sigma]$ for each of the two spatial directions. One MC time unit (cycle) is determined by N trial displacement moves, where in each move a particle is randomly chosen and displaced by Δ. At each area fraction between $\phi = 0.05$ and $\phi = 0.69$, the system is equilibrated for 10^6 MC cycles where the first 50000 cycles are performed at constant pressure [48] and then the remaining cycles at constant volume. Then, for a given value of ϕ, the equilibration is followed by production runs over 5×10^7 cycles.

Results and discussion.—We consider the mean-squared displacement (MSD) of a tagged particle, $\delta r^2(t)$ via $\delta r^2(t) = \langle[\mathbf{r}_t(t) - \mathbf{r}_t(0)]^2\rangle$, where $\mathbf{r}_t(t)$ is the position of a tagged particle at time t and $\langle\ldots\rangle$ denotes the average over all particles in the system and over different time origins. The short- and long-time self-diffusion coefficients are determined from the initial and long-time behavior of the MSD as

$$D_S = \lim_{t\to 0}\frac{\delta r^2(t)}{4t} \quad \text{and} \quad D_L = \lim_{t\to\infty}\frac{\delta r^2(t)}{4t}. \qquad (1)$$

The self-diffusion coefficient at infinite dilution, D_0, for both values of σ is determined using a linear extrapolation of $D_S(\phi)$ to $\phi = 0$. In Fig. 1, the MSDs from the experiment and simulation are shown for a range of area fractions. To allow for a direct comparison between experiment and simulation, lengths are expressed in units of the particle diameter σ and time in units of σ^2/D_0. Note that by rescaling the data with the *constant* D_0, we remove only trivial hydrodynamic effects, i.e., those associated with the movement of a single particle in a solvent.

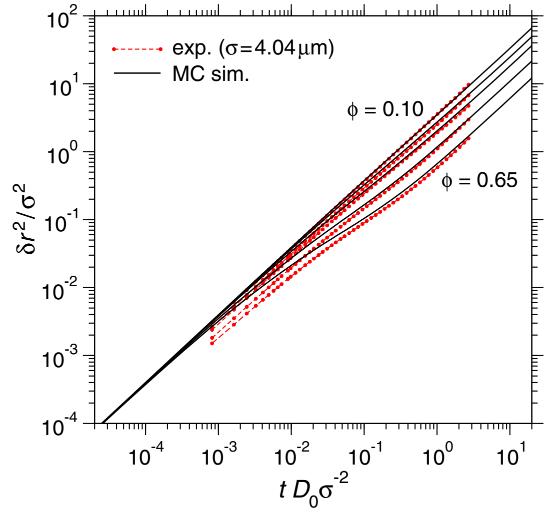

FIG. 1 (color online). Mean-squared displacements in units of the particle diameter σ from experiment with $\sigma = 4.04\ \mu$m (symbols) and simulation (lines) as a function of scaled time, tD_0/σ^2, for the area fractions $\phi = 0.1$, 0.25, 0.39, 0.56, and 0.65.

At all area fractions, the MSDs show a linear regime at short and long times, indicating the occurrence of short-time and long-time diffusive motion. As the area fraction is increased, there is the onset of a plateau at intermediate times due to caging of the tagged particle by the shell of its neighboring particles [49]. Figure 1 clearly shows that at long times, there is quantitative agreement between the MSDs of the experiment and those of the simulation. The same agreement between experiment and simulation is also evident in the variation with ϕ of the long-time self-diffusion coefficient D_L scaled by D_0, which we plot in Fig. 2. This is in contrast to the behavior at short times, where the MSDs of the experiment show a ϕ dependence while those of the simulation are independent of the area fraction.

The differing short-time behavior of the experiment and the simulation can be simply explained by considering the interparticle interactions involved. In the short-time regime, hydrodynamic interactions dominate [26,30,33–35]. As the only interparticle interactions present in the simulation are direct interactions, there is thus no dependence on ϕ at short times. In contrast to this, in the experiment the variation of D_S with ϕ is ascribed to the HI between the particles and/or the interplay of these interactions with other surfaces present such as the wall of the sample container [26,33–35]. The dependence of D_s upon ϕ, shown in Fig. 2, is well described by a linear fit according to $D_S/D_0 = (1 - 0.85\phi)$. The coefficient 0.85 is

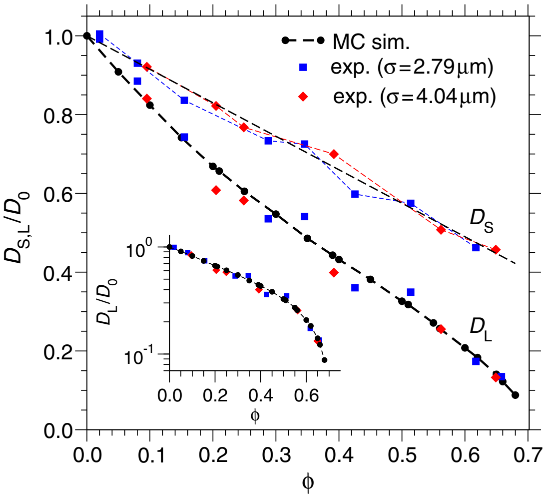

FIG. 2 (color online). Short- and long-time self-diffusion coefficient $D_{S,L}/D_0$ as a function of the area fraction ϕ for the experiment (D_S and D_L) for two different particle diameters $\sigma = 2.79\ \mu$m and 4.04 μm, and the MC simulation (D_L). The dashed line is a fit to the experimental data for D_S according to $D_S/D_0 = (1 - 0.85\phi)$. The inset shows D_L/D_0 as a function of ϕ in a semilogarithmic plot. Note that for low area fractions, $D_L/D_0 \approx 1$–1.74ϕ.

significantly smaller than that expected for $D_S(\phi)$ in 3D [50], consistent with earlier studies of quasi-2D colloidal systems [26,34].

The variation of D_S in the experiment defines an area-fraction-dependent particle mobility associated with nontrivial hydrodynamic effects, i.e., hydrodynamic interactions, and hence the presence of a ϕ-dependent, fundamental time scale of motion in the system. It is widely thought that the ϕ dependence of the long-time self-diffusion coefficient should reflect this short-time particle mobility in addition to the effect of direct interactions between particles. As such, it has been suggested that D_L can be expressed as [43,44]

$$D_L = D_S F_{DI}. \tag{2}$$

Here, F_{DI} is a function solely dependent on the direct interactions and $D_S = D_0 f(\phi)$, where $f(\phi)$ is a function that accounts for the nontrivial hydrodynamic effects, i.e., HI, on D_L. The direct hard-core interactions in the simulation and the experiment are identical, as confirmed by the excellent agreement between the simulated and experimental $g(r)$ shown in the inset of Fig. 4. As such, F_{DI} is identical for the simulation and the experiment, and Eq. (2) may be tested by determining the ratio D_L/D_S as a function of ϕ. In Fig. 3 we plot this ratio for both the experiment and the simulation (where $D_S = D_0$). Substantial deviations between D_L/D_S of the experiment and simulation are seen, indicating the failure of Eq. (2). This directly indicates that the effect of hydrodynamics cannot be fully captured by the short-time self-diffusion coefficient as in Refs. [43,44].

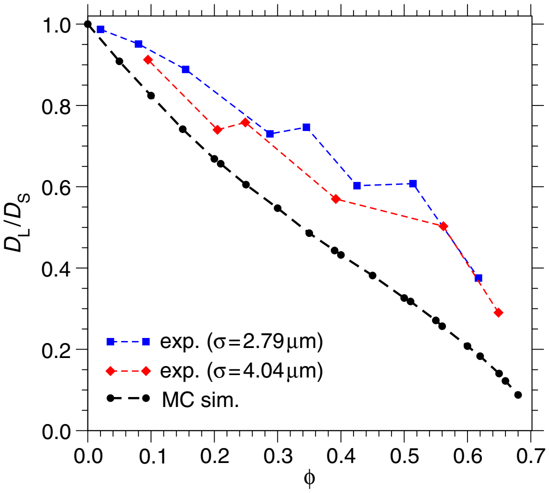

FIG. 3 (color online). The ratio D_L/D_S as a function of the area fraction ϕ for our experiments and MC simulation. Note that for the simulation, $D_S = D_0$.

More surprisingly, for our experimental system, the reduced short-time particle mobility seems to have no effect on the behavior of the long-time self-diffusion coefficient. This is demonstrated by the striking quantitative agreement between the long-time self-diffusion coefficients of the experiment (with solvent) and those of the simulation (without solvent), indicating that the reduction in the diffusion coefficient with increasing ϕ is that expected from the action of direct interactions alone. In other words, the hydrodynamic interactions that lead to the variation of the short-time diffusion coefficient are *effectively* absent with respect to the ϕ dependence of the long-time self-diffusion coefficient. Similar observations that HI have only a very small effect on the long-time self-diffusion coefficient have been made in earlier studies of hard disks [51] and 3D hard sphere fluids [52–54]. Note that the data of Ref. [54] are also incompatible with a scaling of the form of Eq. (2), which suggests that our findings are not a unique result of the experimental geometry.

The simplest explanation for this phenomenon is that the behavior at long times is dominated by the direct hard-core interactions and thus does not reflect the strong dependence of the short-time self-diffusion coefficient on ϕ. Alternatively, HI may contribute to the diffusive behavior at long times but in a more complex manner than can be predicted from the short-time self-diffusion coefficient. For example, the observed agreement between our experiment and simulation results could be described by an expression of the form of Eq. (2), if an extra multiplicative term on the right-hand side of Eq. (2), F_{HI}, was added to compensate for the slowing of the diffusion of particles by HI at short times. Importantly, this term must then *exactly* cancel with D_S for all area fractions, i.e., $F_{\mathrm{HI}} = D_0/D_S$. If this were the case, it would be very remarkable and certainly deserve further study.

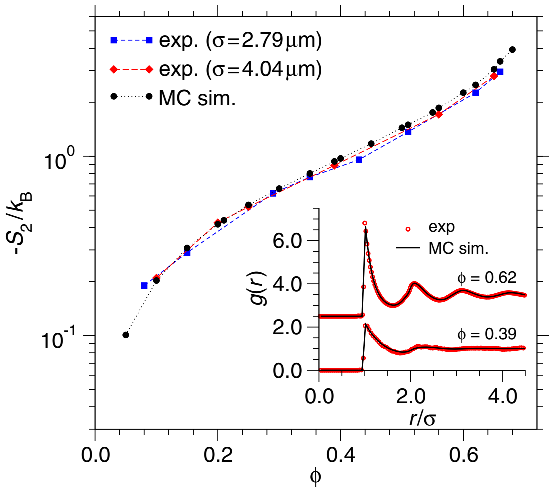

FIG. 4 (color online). The excess entropy $-S_2/k_B$ [Eq. (3)] as a function of area fraction ϕ for the MC simulation and both experimental systems. The inset shows radial distribution functions $g(r)$ from experiment (symbols) and simulation (lines) for $\phi = 0.39$ ($\sigma = 4.04\ \mu$m) and $\phi = 0.62$ ($\sigma = 2.79\ \mu$m). Note that the $g(r)$ for $\phi = 0.62$ is shifted upwards by 2.5.

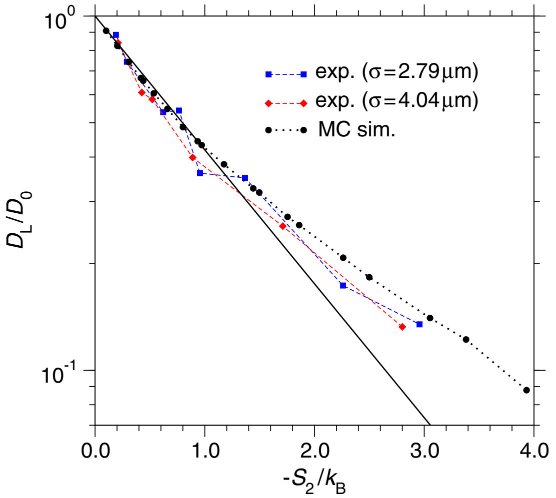

FIG. 5 (color online). Scaled long-time self-diffusion coefficient D_L/D_0 as a function of the excess entropy $-S_2/k_B$ from the MC simulation and the experiment for particle diameters $\sigma = 2.79\ \mu$m and $4.04\ \mu$m, as indicated. The solid line corresponds to Eq. (4) with $\alpha = 0.87$, applicable at low ϕ.

The excellent structural [22] and dynamic characterization of our system at long times makes it an ideal testing ground for a recent attempt to establish a link between the long-time self-diffusion coefficient and the excess entropy S_2, which reflects the structure of fluids, as described on a pair level by the radial distribution function $g(r)$ [3–13]. For a 2D system, the first term of the excess entropy arising from pair interactions is defined by [55]

$$S_2 = -\frac{4k_B\phi}{\sigma^2}\int_0^\infty [g(r)\ln(g(r)) - (g(r)-1)]r\mathrm{d}r. \quad (3)$$

In a recent experimental study for a colloidal fluid in a quasi-2D geometry, it has been claimed that there is a simple relation between D_L/D_0 and S_2, given by

$$D_L/D_0 = \exp(\alpha S_2/k_B), \quad (4)$$

where α is a constant that accounts for the effects of direct interactions and HI [5]. The value of α was found to be dependent on the type of interface and interparticle potential, with deviations of α from unity ascribed to differing HI [5].

In Fig. 4 we show S_2 for the experiment and simulation as a function of ϕ. The very good agreement results from the excellent agreement of the corresponding $g(r)$, shown in the inset of Fig. 4. Any small deviations arise from difficulties associated with the experimental measurement of $g(r)$ and, in particular, the determination of the contact value [22]. In Fig. 5 we show D_L/D_0 as a function of S_2 in a semilog plot for our experimental data and simulation. Again, very good agreement between experiment and simulation is found, and our results are also consistent in magnitude with those of Ref. [5]. Nevertheless, our data suggest that a single scaling law for the long-time self-diffusion coefficient of the form of Eq. (4), which would be linear in this representation, cannot be employed over the whole range of ϕ [4,11,12].

It is possible, however, to apply Eq. (4) in the limit of low area fractions. In this limit, $D_L/D_0 \approx 1 - 0.87(-S_2/k_B)$, which follows from the low ϕ limits of $-S_2/k_B = 2\phi$ and $D_L/D_0 \approx 1$–1.74ϕ (Fig. 2), respectively. This corresponds to a value of $\alpha = 0.87$ in Eq. (4) for low ϕ, which is shown in Fig. 5 as a solid line. While this describes the data well for $\phi < 0.4$, clear deviations from this expression are seen at high ϕ. In this limit, Eq. (4) is only applicable if a prefactor is introduced. By doing so, we find that $\alpha = 0.54$ and 0.58 for the 2.79 μm and 4.04 μm particles, respectively, with a prefactor of 0.66. This indicates that for a system dominated by direct interactions, Eq. (4) with $\alpha = 1$ does not hold. Furthermore, it also demonstrates that a deviation of α from unity is not necessarily the result of HI, as we have shown that these effectively do not affect the area fraction dependence of the long-time self-diffusion coefficient.

Conclusions.—We have compared the short- and long-time self-dynamics of a quasi-2D colloidal system to those of a MC simulation of hard disks. The short-time self-diffusion coefficient from the simulation is independent of the area fraction while that from the experiment strongly varies with the area fraction, indicating that for the experiment, hydrodynamic interactions are important at short times. In contrast, the experimental long-time self-diffusion coefficient scaled by D_0 is in quantitative agreement with that obtained from the simulation. This quantitative agreement shows that the reduction in particle mobility at short times in the experiment does not lead to a proportional reduction of the long-time self-diffusion coefficient and, more surprisingly, that at long times, hydrodynamic interactions are effectively absent. As our system is structurally and dynamically well understood at long times, we have used it to test the relation between the configurational excess entropy and the long-time self-diffusion coefficient and have not found a simple exponential relation between these quantities for all fluid area fractions.

We thank Dirk Aarts, Ard Louis, and Yael Roichman for useful discussions. J. H. and R. E. R. acknowledge the DFG research unit FOR-1394 “Nonlinear response to probe vitrification” (HO 2231/7-2), J. H. and R. P. A. D. the Royal Society, and A. L. T. and R. P. A. D. the EPSRC and the ERC (ERC Starting Grant No. 279541-IMCOLMAT) for financial support. R. E. R. acknowledges financial support from Conicyt/Fondap 15130015 and DIUBB 151507 4/R.

---

[*] roel.dullens@chem.ox.ac.uk
[†] horbach@thphy.uni-duesseldorf.de

[1] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Oxford University Press, Oxford, 1994).
[2] K. Binder and W. Kob, *Glassy Materials and Disordered Solids* (World Scientific, Singapore, 2011).
[3] M. Dzugutov, Nature (London) **381**, 137 (1996).
[4] Y. Rosenfeld, J. Phys. Condens. Matter **11**, 5415 (1999).
[5] X. Ma, W. Chen, Z. Wang, Y. Peng, Y. Han, and P. Tong, Phys. Rev. Lett. **110**, 078302 (2013).
[6] J. J. Hoyt, M. Asta, and B. Sadigh, Phys. Rev. Lett. **85**, 594 (2000).
[7] G. X. Li, C. S. Liu, and Z. G. Zhu, Phys. Rev. B **71**, 094209 (2005).
[8] W. P. Krekelberg, M. J. Pond, G. Goel, V. K. Shen, J. R. Errington, and T. M. Truskett, Phys. Rev. E **80**, 061205 (2009).
[9] A. Samanta, S. M. Ali, and S. K. Ghosh, Phys. Rev. Lett. **87**, 245901 (2001).
[10] P. Holmqvist, Langmuir **30**, 6678 (2014).
[11] C. Kaur, U. Harbola, and S. P. Das, J. Chem. Phys. **123**, 034501 (2005).
[12] J.-L. Bretonnet, J. Chem. Phys. **117**, 9370 (2002).
[13] C.-H. Wang, S.-H. Yu, and P. Chen, Phys. Rev. E **91**, 060201 (2015).
[14] P. Egelstaff, *An Introduction to the Liquid State* (Oxford University Press, Oxford, 1994).
[15] A. Meyer, S. Stüber, D. Holland-Moritz, O. Heinen, and T. Unruh, Phys. Rev. B **77**, 092201 (2008).
[16] J. Horbach, R. E. Rozas, T. Unruh, and A. Meyer, Phys. Rev. B **80**, 212203 (2009).
[17] A. Meyer, Phys. Rev. B **81**, 012102 (2010).
[18] E. R. Weeks and D. A. Weitz, Phys. Rev. Lett. **89**, 095704 (2002).
[19] F. Evers, C. Zunke, R. D. L. Hanes, J. Bewerunge, I. Ladadwa, A. Heuer, and S. U. Egelhaaf, Phys. Rev. E **88**, 022125 (2013).
[20] T. O. E. Skinner, S. K. Schnyder, D. G. A. L. Aarts, J. Horbach, and R. P. A. Dullens, Phys. Rev. Lett. **111**, 128301 (2013).
[21] T. O. E. Skinner, D. G. A. L. Aarts, and R. P. A. Dullens, Phys. Rev. Lett. **105**, 168301 (2010).
[22] A. L. Thorneywork, R. Roth, D. G. A. L. Aarts, and R. P. A. Dullens, J. Chem. Phys. **140**, 161106 (2014).
[23] K. Zahn, J. M. Méndez-Alcaraz, and G. Maret, Phys. Rev. Lett. **79**, 175 (1997).
[24] M. Brunner and C. Bechinger, Europhys. Lett. **63**, 791 (2003).
[25] S. Mazoyer, F. Ebert, G. Maret, and P. Keim, Europhys. Lett. **88**, 66004 (2009).
[26] Y. Peng, W. Chen, T. M. Fischer, D. A. Weitz, and P. Tong, J. Fluid Mech. **618**, 243 (2009).
[27] B. Cui, B. Lin, and S. A. Rice, J. Chem. Phys. **114**, 9142 (2001).
[28] A. H. Marcus, J. Schofield, and S. A. Rice, Phys. Rev. E **60**, 5725 (1999).
[29] M. D. Carbajal-Tinoco, G. Cruz de León, and J. L. Arauz-Lara, Phys. Rev. E **56**, 6962 (1997).
[30] J. Santana-Solano, A. Ramírez-Saito, and J. L. Arauz-Lara, Phys. Rev. Lett. **95**, 198301 (2005).
[31] W. Kegel and A. van Blaaderen, Science **287**, 290 (2000).
[32] C. A. Murray and D. H. Van Winkle, Phys. Rev. Lett. **58**, 1200 (1987).
[33] B. Bonilla-Capilla, A. Ramírez-Saito, M. A. Ojeda-López, and J. L. Arauz-Lara, J. Phys. Condens. Matter **24**, 464126 (2012).
[34] V. N. Michailidou, G. Petekidis, J. W. Swan, and J. F. Brady, Phys. Rev. Lett. **102**, 068302 (2009).
[35] J. Santana-Solano and J. L. Arauz-Lara, Phys. Rev. Lett. **87**, 038302 (2001).
[36] R. Pesché and G. Nägele, Phys. Rev. E **62**, 5432 (2000).
[37] J. Bleibel, A. Domínguez, F. Günther, J. Harting, and M. Oettel, Soft Matter **10**, 2945 (2014).
[38] B. Cui, H. Diamant, B. Lin, and S. A. Rice, Phys. Rev. Lett. **92**, 258301 (2004).
[39] R. Pesché, M. Kollmann, and G. Nägele, J. Chem. Phys. **114**, 8701 (2001).
[40] R. Pesché and G. Nägele, Europhys. Lett. **51**, 584 (2000).
[41] H. Löwen, J. Phys. Condens. Matter **4**, 10105 (1992).
[42] B. Cichocki and B. U. Felderhof, J. Phys. Condens. Matter **6**, 7287 (1994).
[43] M. Medina-Noyola, Phys. Rev. Lett. **60**, 2705 (1988).
[44] J. F. Brady, J. Fluid Mech. **272**, 109 (1994).
[45] J. Crocker and D. Grier, J. Colloid Interface Sci. **179**, 298 (1996).
[46] B. Cichocki and K. Hinsen, Physica (Amsterdam) **166A**, 473 (1990).
[47] E. Sanz and D. Marenduzzo, J. Chem. Phys. **132**, 194102 (2010).
[48] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic Press, San Diego, 2002).
[49] W. Götze, *Complex Dynamics of Glass-Forming Systems* (Oxford University Press, Oxford, 2009).
[50] G. K. Batchelor, J. Fluid Mech. **74**, 1 (1976).
[51] E. Falck, J. M. Lahtinen, I. Vattulainen, and T. Ala-Nissilä, Eur. Phys. J. E **13**, 267 (2004).
[52] A. van Blaaderen, J. Peetermans, G. Maret, and J. Dhont, J. Chem. Phys. **96**, 4591 (1992).
[53] G. Batôt, V. Dahirel, G. Mériguet, A. A. Louis, and M. Jardat, Phys. Rev. E **88**, 043304 (2013).
[54] A. Tomilov, A. Videcoq, T. Chartier, T. Ala-Nissilä, and I. Vattulainen, J. Chem. Phys. **137**, 014503 (2012).
[55] A. Baranyai and D. J. Evans, Phys. Rev. A **40**, 3817 (1989).