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Solvent hydrodynamics speed up crystal nucleation in suspensions of hard spheres

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Abstract – We present a computer simulation study on the crystal nucleation process in suspensions of hard spheres, fully taking into account the solvent hydrodynamics. If the dynamics of crystallization in this system were purely diffusive, the crystal nucleation rate would be inversely proportional to the solvent viscosity. However, we observe that the nucleation rate is enhanced at high viscosities with respect to the diffusive behaviour. This effect might explain the large discrepancy between the nucleation rates obtained by simulation and experiment that have been reported in the literature so far.

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Introduction. – Colloids are widely used as model systems to study fundamental questions of statistical mechanics. Over the past twenty-five years the phase behaviour, phase transition kinetics and glass transition of colloidal suspensions have been observed in numerous experiments and modelled by means of theory and simulations [1–7]. In addition to the interest in colloids in their own right, it is often argued that colloids could serve as model systems for atomic and molecular substances [8,9]. Indeed, colloids can be designed to resemble atoms in many aspects of their equilibrium structure and phase behaviour. But there is a major difference in their dynamics: Colloidal particles are suspended in a solvent. They interact directly with each other (*e.g.* by excluded volume) as well as indirectly by means of momentum transfer via the solvent (“hydrodynamic interaction”) [10]. The question we would like to address in this paper is how hydrodynamic interactions influence crystallization kinetics in colloidal suspensions.

Since the pioneering experiments of Pusey and van Meegen in the 1980s [11] crystal nucleation in hard spheres has been observed in numerous experiments and simulations. Strikingly, the nucleation rate densities obtained by computer simulation differ significantly from those observed in experiments [12–16]. The reason for this discrepancy has not been understood yet. Up to now, no

simulation study on this topic has taken into account hydrodynamic interactions [14–17]. Thus, it makes sense to ask whether the solvent, which is inevitably present in the experiments, is the reason for the discrepancy.

Nucleation is commonly described by classical nucleation theory and extensions thereof. This type of theory is based on transition state theory, *i.e.* the assumption that there is a small number of macroscopic observables which vary slowly during the phase transition process (*e.g.* the size of the largest crystallite), while all other degrees of freedom are equilibrated very quickly and can thus be considered Boltzmann-distributed. The nucleation rate density $I(t)$ is given by

$$I(t) = \kappa \exp(-\beta\Delta G^*) \quad (1)$$

where ΔG^* is the height of the free-energy barrier associated with the formation of a critical nucleus and κ is a kinetic prefactor. In the context of crystallization of a colloidal suspension the transition state theory approach implies that the transport properties of the solvent only enter the kinetic prefactor, because the height of the nucleation barrier is determined completely by the equilibrium properties of the colloidal system. If, in addition, the process by which colloids are attached to the crystal nucleus is purely diffusive and non-cooperative, the self-diffusion

time of the colloids is the only relevant time-scale entering the kinetic pre-factor. In this paper we will present a test of these assumptions.

Simulation methods and analysis. – To simulate hard spheres suspended in a solvent, we used a combination of an event-driven molecular-dynamics algorithm [18–21] for the spheres and multiparticle-collision dynamics (MPCD) [22,23] as a mesoscopic solvent model to account for the hydrodynamic interactions. The basic idea of a MPCD algorithm is to transport momentum through the system by means of point particles while satisfying the conservation laws of mass, energy and momentum locally. The motion of the particles consists of free streaming and multiparticle collisions. In the free-streaming step, all point particles are propagated ballistically for a time-interval of duration h . In the subsequent collision step, their velocities are randomized according to the protocol described in ref. [24]. As the duration h sets the speed at which the velocities are randomized, the solvent viscosity can be controlled by varying h . In order to measure the solvent viscosity η for a given value of h , we imposed a Poiseuille flow between two planar walls. From the resulting parabolic velocity field we extracted η .

The colloidal spheres were modelled as hard spheres of diameter a and mass m and they took part in the collision step. We present all data in units of a , m and the thermal energy $k_B T$. Solvent viscosities range between approximately $4\sqrt{mk_B T}/a^2$ and $70\sqrt{mk_B T}/a^2$. Translated to an experimental system with colloidal particles of radius 420 nm suspended in a solvent of mass density 1 g cm^{-3} at room temperature, these viscosities correspond to a range from $8.9 \cdot 10^{-6}\text{ Pa} \cdot \text{s}$ to $1.5 \cdot 10^{-4}\text{ Pa} \cdot \text{s}$.

We have simulated systems containing 8240 hard spheres at volume fractions, $\phi = 0.537, 0.539$ and 0.544 . The starting configurations were prepared in the supersaturated liquid state and we verified that they did not contain crystalline precursors. Then we simulated 40 independent trajectories per value of solvent viscosity until crystallization was reached in all cases. For $\phi = 0.537$ and 0.539 we observe an induction period that is long compared to the diffusion times of the system followed by a regime of rapid growth. Hence, for these two volume fractions, we are confident that we are dealing with nucleation.

We identified crystallites by means of the “ q_6 -bond order parameter” [25,26]. For a sphere i with $n(i)$ neighbors, the local 6-fold bond-orientational order is characterized by

$$\bar{q}_{6m}(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{6m}(\vec{r}_{ij}), \quad (2)$$

where \vec{r}_{ij} is the position vector between a sphere i and its neighbour j and $Y_{6m}(\vec{r}_{ij})$ are the spherical harmonics for $m = -6, \dots, 6$. A vector $\vec{q}_6(i)$ is assigned to each sphere, the elements of which are defined as

$$q_{6m}(i) := \frac{\bar{q}_{6m}(i)}{\left(\sum_{m=-6}^6 |\bar{q}_{6m}(i)|^2\right)^{1/2}}. \quad (3)$$

If a sphere had more than 9 neighbours with $\vec{q}_6(i) \cdot \vec{q}_6^*(j) > 0.7$, it was considered “crystalline”.

Once a simulation run had produced a crystalline cluster consisting of more than 80 spheres, it definitely did not fluctuate back into the liquid state. Thus, we used this value to locate the nucleation time. To test the validity of this criterion, we performed a committor analysis for two values of viscosity ($\eta = 4.17\sqrt{mk_B T}/a^2$ and $\eta = 63.93\sqrt{mk_B T}/a^2$). We found that in both cases a cluster size of ca. 30 spheres corresponds to a 50% probability for subsequent full crystallization. As the growth process is very fast compared to the induction period, the induction times extracted from the committor analysis hardly differ from those obtained by means of the “80-particle criterion”. The conclusions that we draw in the following are not affected by using the latter method. We took the arithmetic mean of the distribution of measured induction times $\langle t_{\text{ind}} \rangle$ to determine the nucleation rate density,

$$I = \frac{1}{V \langle t_{\text{ind}} \rangle}, \quad (4)$$

(where V is the volume of the system), and its standard deviation to determine the error bars.

We did not wish to make any assumptions on the evolution of the density of states or the length of correlation times involved in the nucleation process. In particular, we wanted to allow for processes that might involve “slow” coordinates other than the size of the largest nucleus. Therefore, we did not use any free-energy-based sampling scheme to speed up the simulations.

Results and discussion. – When simulation data for nucleation in colloids is compared with experiments—or when experiments of chemically different composition are compared to one another—the solvent is usually taken into account by normalizing the nucleation rate density with respect to either the long-time self-diffusion coefficient in the dense suspension, D_L , or in the infinitely dilute suspension, D_0 . (As shown above, this procedure assumes that transition state theory can be applied and that the attachment dynamics are purely diffusive and non-cooperative.)

Figure 1 shows the long-time self-diffusion constants extracted from simulations of the infinitely dilute system, D_0 , and the supersaturated suspension, D_L at varying solvent viscosity η . Both diffusion constants follow the expected $1/\eta$ -behaviour. Hence we are confident that the MPCD approach correctly captures the hydrodynamics of the system.

Figure 2 shows the nucleation rate density *vs.* the solvent viscosity η . If the time-scale entering the kinetic pre-factor were determined by diffusion of the spheres only, the nucleation rate density would drop as $1/\eta$. The simulation data for the two lower volume fractions in fig. 2 clearly deviate from a $1/\eta$ -law for high viscosities. Hence we conclude that hydrodynamic interactions speed up the

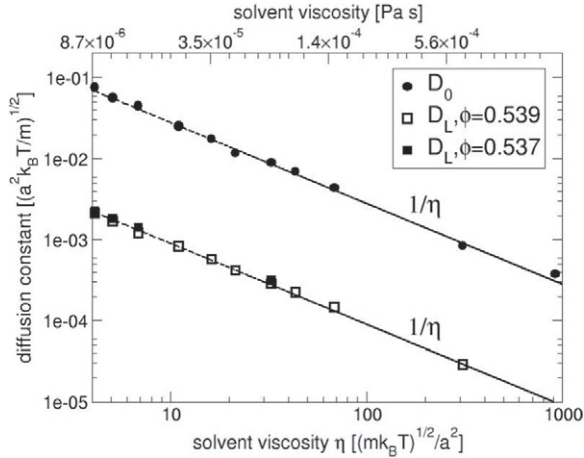


Fig. 1: Diffusion constants in the infinitely dilute system, D_0 , and in the dense suspension, D_L .

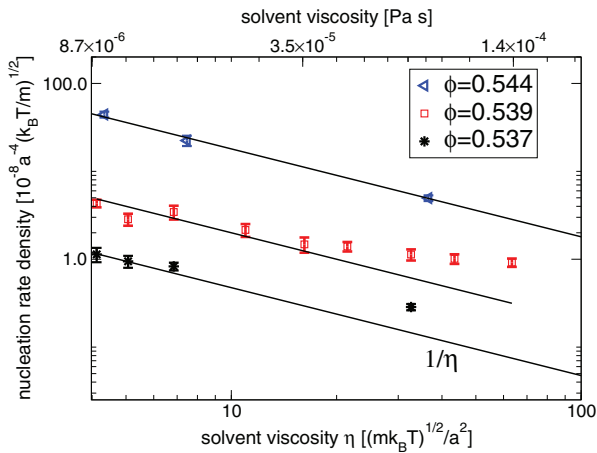


Fig. 2: (Colour on-line) Nucleation rate densities as a function of solvent viscosity. If the only relevant time-scale were the diffusion time, the rates would drop as $1/\eta$.

nucleation process¹. This implies that nucleation rate densities for systems with different solvent viscosities cannot be superposed by scaling out the diffusion time.

Experimentally, hard-sphere suspensions are synthesized in various ways: Common systems are polystyrene spheres suspended in water, and sterically stabilized polymethylmethacrylate (PMMA) spheres in an organic liquid such as decalin. Typical solvent viscosities are in the range of $1 \cdot 10^{-3}$ – $3 \cdot 10^{-3}$ Pa · s. Figure 3 shows a compilation of nucleation rate densities obtained by experiment (closed symbols) [12,28–31] and computer simulation without solvent hydrodynamics (open symbols and lines) [14,15]. The experimental data is subject to large systematic errors both in the colloid concentration [9] and in the nucleation

¹A recent study on seeded crystal growth in suspensions of soft colloids confirms that solvent hydrodynamics have an effect on growth rates beyond the trivial dependence of the diffusion time. However, due to the different interaction potential and surface curvature, in this case the rates were decreased rather than increased [27].

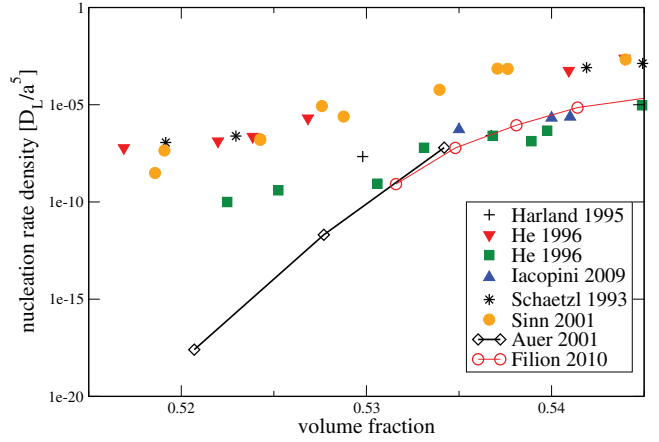


Fig. 3: (Colour on-line) Nucleation rate densities scaled by D_L from experiment (closed symbols) [12,28–31] and simulation (open symbols, lines) [14,15].

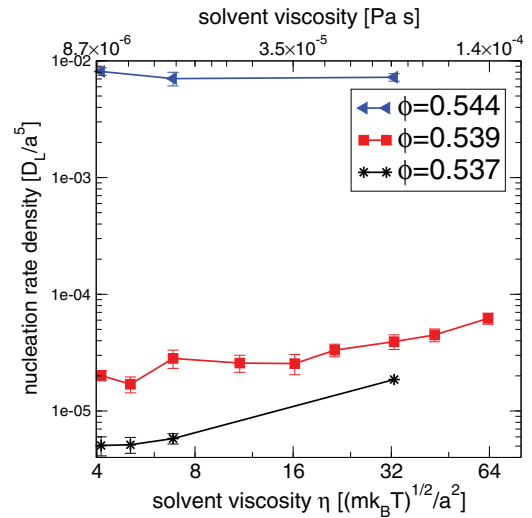


Fig. 4: (Colour on-line) Nucleation rate densities scaled by D_L vs. solvent viscosity. The hydrodynamic effect increases with decreasing supersaturation.

rate density. Therefore, results given by different research groups can differ by orders of magnitude, although the statistical error of the individual experiments is less than one order of magnitude. Common to all experimental data sets, however, is the slope which is clearly less steep than the slope of the computer simulation results. Hence, the smaller the supersaturation, the larger becomes the discrepancy between experiment and simulation (note that the y -axis is logarithmic.).

Figure 4 shows our simulation data rescaled with respect to D_L (rescaling with respect to D_0 instead of D_L would just shift the curves by a constant, see fig. 1). We find that the enhancement of the nucleation rate is larger for smaller volume fractions than for higher volume fractions. This trend is consistent with the increasing gap between experiment and simulation in fig. 3.

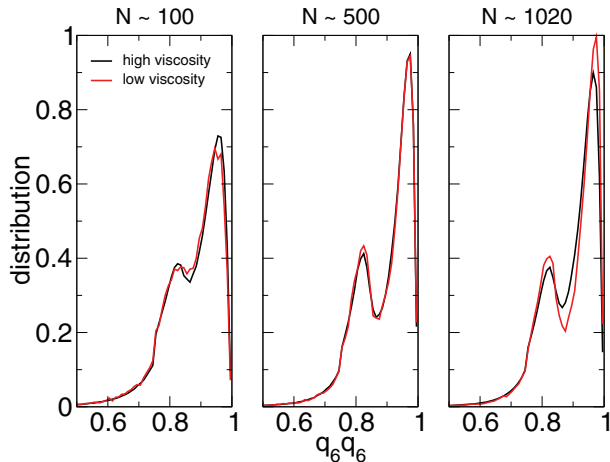


Fig. 5: (Colour on-line) Distributions of q_6q_6 for different cluster sizes at $\eta = 4.17\sqrt{mk_B T}/a^2$ and $\eta = 63.93\sqrt{mk_B T}/a^2$.

Finally we would like to discuss whether the nucleation process can be described in terms of transition state theory, *i.e.* whether the nucleation rate consists of a free-energy-barrier term, which is independent of the kinetics, and a prefactor which contains the solvent hydrodynamics. As the nucleation rate densities are affected by hydrodynamic interactions, one could expect to observe differences in the sizes, shapes or structures of the crystallites that form, too. We analysed the structures of the growing crystallites in terms of their q_6 -bond order [25,26]. Figure 5 shows $\vec{q}_6(i) \cdot \vec{q}_6(j)$ for pairs of particles i and j in clusters of equal sizes obtained at different solvent viscosities. The crystallites are very similar in structure. Within the statistical accuracy, the radii of gyration of the crystallites did not differ (data not shown). When performing the committer analysis for the highest and the lowest viscosity we did not find any difference in the critical cluster size, shape or structure, either. As the dynamics of the solvent do not influence the properties of the critical nucleus, we conclude, that the nucleation process can be described in terms of a free-energy barrier and a kinetic prefactor.

Conclusion. – In summary, we have simulated crystallization from a supersaturated liquid suspension of hard spheres taking into account the solvent hydrodynamics. We find that kinetics need to be taken with care when one studies phase transitions in colloids. Contrary to what has been assumed in the literature so far, the crystal nucleation rate densities for hard spheres do not drop as the inverse of the solvent viscosity. The attachment dynamics are not purely diffusive, the kinetic pre-factor is affected by hydrodynamic interactions. It is thus not possible to superpose nucleation rate densities obtained from systems with different solvent viscosities by scaling out the diffusion time.

It would be very interesting to see a test of our observations in an experiment on hard spheres suspended in

a solvent of a different chemical composition from that commonly used.

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