Effect of hydrodynamic interactions on the lifetime of colloidal bonds

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Abstract

We use analytical theory and numerical simulation to study the role of short-range hydrodynamics (lubrication forces) in determining the lifetime of colloidal bonds. Such insight is useful in understanding many aspects of colloidal systems, such as gelation, nucleation, yielding and rejuvenation, and as a paradigm for diffusion-controlled dissociation reactions in liquids. Our model system consists of spherical particles with an attractive square-well potential of variable width δ. We find that the predicted colloidal bond lifetimes can be substantially increased upon inclusion of lubrication forces, to an extent which depends on the attraction range. An analytical law is derived which predicts this enhancement as a function of the well width, in quantitative agreement with simulation data. For sufficiently short-ranged attraction, lubrication forces dramatically enhance the drag on two bonded particles, leading to reduced effective diffusion coefficients and hence longer bond lifetimes. This effect disappears upon increasing the width of the attractive wells beyond a length-scale comparable to the particle diameter. The simulation further suggests that the role of lubrication forces becomes less important as confinement is increased, i.e. upon approaching the supersaturation limit, $\phi \approx 0.5$, where caging effects become important. Our findings complement recent

studies of the role of long-range hydrodynamic interactions, contributing to a comprehensive description of the subtle link between hydrodynamics and bonding in attractive colloids.

Introduction

Yield-stress materials, such as gels, are ubiquitous in diverse areas of industry and nature.[1] Their complex mechanical properties make them suitable for applications such as in healthcare, cosmetics, and foodstuffs,[2] while simultaneously making manufacture and processing challenging and empirical. Of particular interest, both as industrial and commercial products and as model systems for fundamental studies, are colloidal gels. Such systems are highly appealing, as the particle-particle interactions may be precisely tuned by modifying the surface chemistry of, for example, PMMA spheres,[3] while the colloids are typically large enough to be seen easily under a confocal microscope.[4]

In the limit of very attractive particles, colloidal suspensions may irreversibly form stable percolating gels at low volume fractions.[5] For more weakly attractive particles binding may be reversible, in which case higher volume fractions are required to achieve percolation, and the kinetic arrest associated with gelation shares features with the colloidal glass transition.[6] In such cases, the bond lifetime is central to determining the timescales over which the gel will yield, creep and flow.[7] Of crucial importance, therefore, is a good understanding of those factors that influence the lifetime of reversible binding in such weakly attractive colloids. Clearly, the depth of the attractive potential influences the bond lifetime, with attractive strengths of order $k_B T$ being sufficiently weak to break and reform under quiescent conditions. Further complicating this, though, is the role of hydrodynamic interactions in setting the particle diffusion coefficients.

The fundamental understanding of this problem is of course also important in the context of molecular diffusion-limited dissociation reactions in liquids, where the dynamics is also overdamped (Brownian) and hydrodynamic interactions can be important for large molecules

and molecular complexes. In this area, a theory of the effect of hydrodynamic interactions on diffusion-limited association rates was developed by Deutch and Felderhof,[8] using long-range hydrodynamics, but the reverse process of dissociation reactions has not been treated. Clearly, one expects short-range hydrodynamics to be more important for the dissociation reaction than for the association reaction, and *vice versa* for the long-range hydrodynamics.

The importance of hydrodynamic interactions (HI) to gelation has now been appreciated,[9] and recent studies have attested to the augmenting role played specifically by long-range hydrodynamic interactions.[10,11] In the present study, we turn the attention to short-range hydrodynamic interactions (lubrication forces),[12] and investigate their influence on the lifetime of colloidal bonds. Our theoretical analysis predicts a strong decrease of the diffusion coefficients of closely-neighbouring particles when lubrication forces are accounted for, which is crucially modulated by the attraction range. This interplay between hydrodynamics and attraction range directly controls the colloidal bond lifetimes.

We simulate a quiescent system of colloidal particles that interact via attractive square wells, and find a quantitative match with the theoretical prediction when comparing results with and without lubrication forces, for low volume fractions. The results show that lubrication forces increase the lifetime of colloidal bonds, and that this effect is most significant in those colloids with short range attractions. Short range attractions bring particles into close proximity, where the lubrication forces diverge. By contrast, the range of proximities over which long range attractions act mean that some neighbouring bonded particles feel large lubrication forces, while many do not. In this case, the typical bond lifetime is only marginally enhanced by the inclusion of lubrication. Furthermore, our simulation model allows us to investigate the competing effects of confinement and lubrication. At high volume fractions, $\phi = 0.50, 0.55$, bond lifetimes are enhanced additionally by many-body confinement imposed by neighbouring particles, which to some extent masks the effects of lubrication.

Analytical theory

Let us consider the case where the bound state is given by an attractive rectangular potential well $U(r)$, such that $U = \text{const} = -\Delta$ for $\sigma < r \leqslant \sigma + \delta$, $U = 0$ for $r > \sigma + \delta$, and $U = \infty$ for $r = \sigma$, where δ and Δ are the width of the well and its depth, respectively, and σ the particle diameter, Fig 1. We assume that lubrication forces affect the particle mobility through the particle diffusion coefficient $D(r) = G(r)D_\infty$, where $G(r)$ is the hydrodynamic viscous lubrication function, $D_\infty = k_B T/(3\pi\mu\sigma/2)$ the Stokes-Einstein formula for mutual diffusion, and μ denotes the solvent viscosity.

In general, lubrication leads to a very low diffusivity when the particles are close to each other due to the incompressible solvent being squeezed in the gap between the two spheres, and ultimately $D = 0$ at $r = \sigma$ which implies that the mobility is zero when the particles are in contact due to the incompressibility of the solvent. Since the hydrodynamic interaction decays as $1/r$, the effect tends to vanish for very long distance where $D(r) \to D_\infty$ as $r \to \infty$.

The friction coefficients, and thus D, for a system of two spheres were calculated analytically by solving the Stokes equations by Stimson and Jeffery.[13] However, since the full theoretical expression is given as an infinite series, for the purpose of analytical calculations it is customary to represent it with the following interpolation formula:[14]

$$G(h) = \frac{6h^2 + 4h}{6h^2 + 13h + 2} \tag{1}$$

where $h = (r - \sigma)/(\sigma/2)$. $D(r)/D_\infty$ using Eq.(1) is plotted in Fig 2 and shows the expected trend.

Here we show how the Kramers escape rate from such a square-well bound state can be calculated upon accounting for two-body hydrodynamic interactions. In the Kramers escape theory, the Smoluchowski diffusion in a field of potential energy is taken as the starting point. The key assumption is made that the potential well is deep enough such that the probability of finding a particle in the well follows the Boltzmann distribution (which
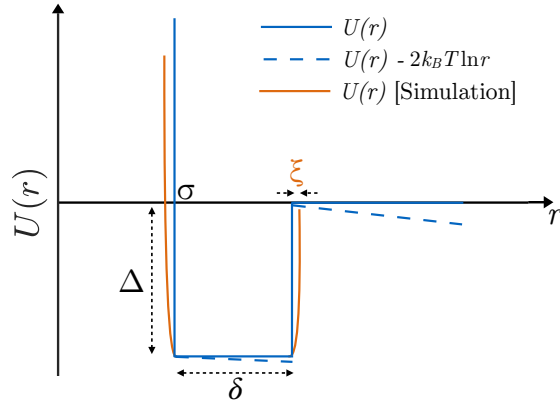
Figure 1: The attractive potential considered in this work. Shown are the square well $U(r)$, the square well adjusted for entropic effects $U(r) - 2\ln r$, and the simulation approximation.

solves the Smoluchowski equation at steady-state). Next, the steady-state flux from the well through a barrier is calculated by integrating the Smoluchowski equation using the assumption above and the assumption that the probability of finding the particle beyond the barrier is low because the potential energy pushes the particle away on its outward trajectory. Clearly, for a purely attractive potential, there is no force that pushes the particle away along the outward direction, and nothing prevents the particle from falling back into the well. This subtle issue has been discussed in Ref.[15] A practical way around this paradox, for dimensions $d > 1$, comes from the metric space in spherical coordinates. With an exact manipulation, the metric factor in the integrals can be written as an effectively repulsive ("dilution entropy") contribution to the potential $U(r)$, as was already discussed in Ref.[16] This procedure reduces the original 3D spherical problem to an effective 1D problem with an effective potential that now features a maximum (the barrier), and now also the second Kramers assumption is satisfied. Finally, the presence of the barrier as a local maximum of the potential energy, allows one to use the saddle-point approximation for the integrals. Below we work in 3D with spherical symmetry, therefore even though there is no barrier, obviously, in our square-well potential, the above trick could be applied. However, as we show below, this is not necessary because the integrals turn out to be analytical solvable for the square-well case.
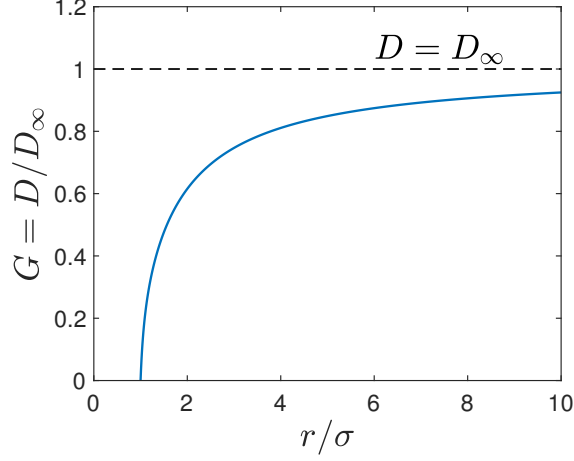
Figure 2: The lubrication correction to the Stokes-Einstein diffusion coefficient according to the formula Eq. (1) which parameterizes the analytical solution of Stimson and Jeffery.

If $n(r,t)$ denotes the probability density of finding the particle at position r and time t (and thus coincides with the mean number density $n = N/V$ at a macroscopic level), the quasi-stationary Smoluchowski (diffusion) equation [17]

$$\frac{\partial n}{\partial t} = \left[\frac{1}{r^2} \frac{d}{dr} r^2 D(r) \left(\frac{1}{k_B T} \frac{dU(r)}{dr} n + \frac{dn}{dr} \right) \right] = 0 \tag{2}$$

yields a current J (of dimensionality [1/time]) of particles diffusing into the spherical surface of radius r. This total current J is constant (r-independent) in the steady state, unlike the vector of flux in this spherical $3D$ geometry; this integrated current is given by

$$J = -(4\pi r^2) D(r) e^{-U(r)/k_B T} \frac{d}{dr} \left[e^{U(r)/k_B T} n(r) \right] \tag{3}$$

where $n(r)$ is the probability density of particles, which need to travel across the interaction potential energy landscape for dissociation, $U(r)$. Following the Kramers method, we integrate Eq.(3) between r^* and C. Here C is some point far away on the radial axis, and r^* is some point inside the well $r^* \lesssim \sigma + \delta$. Upon assuming that the probability of finding a particle in the well has thermalised at steady-state before the escape can take place, we have $\int_{r^*}^{C} d[e^{U(r)/k_B T} n(r)] \approx [e^{U(r)/k_B T} n(r)]_{r^*}$.

Assuming that the probability density becomes negligible at $r = C$ far away on the r axis, we can express the constant current as

$$J = \frac{e^{U(r^*)/k_BT}n(r^*)}{\int_{r^*}^{C} \frac{e^{U(r)/k_BT}}{4\pi D(r)r^2}dr}. \tag{4}$$

The steady-state probability density in the well is given approximately by the stationary Boltzmann distribution $n(r) = n(r^*)e^{-[U(r)-U(r^*)]/k_BT}$. Thus the probability of finding the particle in the 3D well is given by integrating the density over the spherical shell of this well, i.e. by integrating up to $\sigma + \delta$:

$$\begin{aligned} p &= \int_{\sigma}^{\sigma+\delta} n(r)\, 4\pi r^2 dr \\ &= n(r^*)e^{U(r^*)/k_BT} \int_{\sigma}^{\sigma+\delta} e^{-U(r)/k_BT} 4\pi r^2 dr\,. \end{aligned} \tag{5}$$

Upon taking $C = \infty$, the Kramers escape time follows as $1/\kappa \equiv p/J$, that is,

$$\frac{1}{\kappa} = \frac{1}{D_\infty} \int_{\sigma}^{\sigma+\delta} e^{-U(r)/k_BT} r^2 dr \int_{\sigma+\delta}^{\infty} \frac{e^{U(r)/k_BT}}{G(r)r^2}dr. \tag{6}$$

This result can be rewritten by introducing a formal identification $U_{\text{eff}} = U(r) - 2k_BT\ln r$, where we just bring the metric factor r^2 into the exponential to give the exactly equivalent form:

$$\frac{1}{\kappa} = \frac{1}{D_\infty} \int_{\sigma}^{\sigma+\delta} e^{-U_{\text{eff}}(r)/k_BT} dr \int_{\sigma+\delta}^{\infty} \frac{e^{U_{\text{eff}}(r)/k_BT}}{G(r)}dr. \tag{7}$$

This expression is exactly identical to the result that one would get in 1D with a potential given approximately by the dashed line in Fig. 1. Physically this means that, in 3D, the particle moving away along the r axis effectively enjoys a larger number of degrees of freedom due to the metric (a sort of dilution entropy) compared to the situation in 1D where the metric factor is equal to 1, as was already pointed out in Ref. [16]

The integrals can be done analytically for the square-well case, which leads to the fol-

lowing analytical expression for the rate of dissociation of a colloidal square well bond in the presence of lubrication forces:

$$\kappa_{HI} = \frac{\frac{3}{2}\frac{\sigma}{(\sigma+\delta)^3-\delta^3}D_\infty e^{-\Delta/k_BT}}{\frac{1}{8}\left[11\ln\left(1+\frac{\delta}{\sigma}\right)-2\ln\frac{\delta}{\sigma}+9\ln\left(\frac{3}{1+3(\delta/\sigma)}\right)\right]} \tag{8}$$

and the lifetime of the colloidal bond is just the inverse of the rate, $\tau_{HI} = 1/\kappa_{HI}$:

$$\tau_{HI} = \frac{\frac{2}{3}\frac{(\sigma+\delta)^3-\delta^3}{\sigma D_\infty}e^{\Delta/k_BT}}{\left\{\frac{1}{8}\left[11\ln\left(1+\frac{\delta}{\sigma}\right)-2\ln\frac{\delta}{\sigma}+9\ln\left(\frac{3}{1+3(\delta/\sigma)}\right)\right]\right\}^{-1}} \tag{9}$$

In the absence of hydrodynamic interactions, one has:

$$\kappa = \frac{\frac{3}{2}\frac{\sigma D_\infty}{(\sigma+\delta)^3-\delta^3}e^{-\Delta/k_BT}}{\frac{1}{1+\delta/\sigma}} = \frac{3}{2}\frac{\sigma(1+\delta/\sigma)D_\infty}{(\sigma+\delta)^3-\delta^3}e^{-\Delta/k_BT} \tag{10}$$

and for the lifetime:

$$\tau = \frac{2}{3}\frac{(\sigma+\delta)^3-\delta^3}{\sigma(1+\delta/\sigma)D_\infty}e^{\Delta/k_BT}. \tag{11}$$

The lifetime of a colloidal bond with hydrodynamic interactions, τ_{HI} is compared with the lifetime in the absence of HI in Fig 3. It is evident that with HI the lifetime of the colloidal bond is significantly larger than without HI, especially for short range attractions. For very long range attraction $\delta > 10\sigma$, instead, the enhancement of the bond lifetime due to HI tends to vanish and there is basically no effect of HI. To better understand the effect of hydrodynamic interactions on the dissociation process, we introduce the following attraction range-dependent (but r-independent!) effective diffusion coefficient for the dissociation process:

$$D_{\text{eff}} = \frac{D_\infty/(1+(\delta/\sigma))}{\frac{1}{8}\left[11\ln\left(1+\frac{\delta}{\sigma}\right)-2\ln\frac{\delta}{\sigma}+9\ln\left(\frac{3}{1+3(\delta/\sigma)}\right)\right]}. \tag{12}$$

With this notation, the lifetime with HI can be written in terms of the lifetime without hydrodynamic interactions where the Stokes-Einstein diffusivity is replaced by the effective

one accounting for HI:

$$\tau_{HI} = \frac{2}{3} \frac{(\sigma + \delta)^3 - \delta^3}{\sigma(1 + \delta/\sigma)D_{\text{eff}}} e^{\Delta/k_B T} = \tau D_\infty / D_{\text{eff}} \tag{13}$$

and therefore:

$$\tau_{HI}/\tau = D_\infty / D_{\text{eff}}. \tag{14}$$

The effect of two-body hydrodynamic interactions is to generate a stronger resistance to Brownian motion, hence $D_{\text{eff}} < D_\infty$ always, and only in the far-field $r \to \infty$ one recovers $D_{\text{eff}} = D_\infty$, because the HI is long-range and vanishes at infinity. In the bond-breakup process, Brownian motion is the driving force which provides the colloidal particle with the kinetic energy fluctuations required to jump over the barrier given by the bonding energy with the other particle. The longer lifetime in the presence of HI is thus explained in terms of a higher friction or higher resistance to Brownian motion caused by HI which effectively reduces the kinetic energy fluctuations that promote bond-breakup. As a consequence, the lifetime of a bond between two colloidal particles can be greatly enhanced, up to a factor 4 for short-ranged attraction, by hydrodynamic interactions.
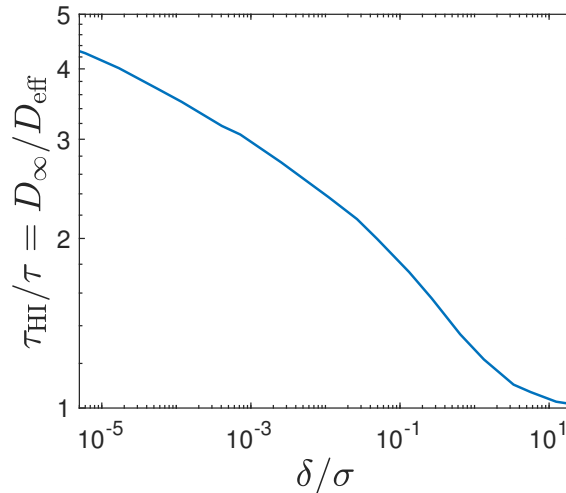

Figure 3: The ratio between the colloidal bond lifetime with HI, τ_{HI}, and the lifetime without HI, τ.

Simulation model and results

We solve the Langevin equation

$$m\frac{d\boldsymbol{v}}{dt} = \boldsymbol{F}_h + \boldsymbol{F}_c + \boldsymbol{F}_b, \tag{15}$$

for a system of 2000 monodisperse particles with radii σ, masses m, velocities $\boldsymbol{v}$ and subject to hydrodynamic $\boldsymbol{F}_h$, contact $\boldsymbol{F}_c$ and Brownian $\boldsymbol{F}_b$ forces.[18] We remain in the limit where the time-scales for relaxation of momentum and position are well-separated. Following Refs.,[19,20] we approximate the full hydrodynamic resistance matrix $\boldsymbol{R}$[21] simply using pairwise, frame-invariant lubrication interactions and we compute just the leading terms

$$\boldsymbol{F}_h = -a_{sq}6\pi\eta_f(\boldsymbol{v}_i - \boldsymbol{v}_j)\cdot\mathbf{n}_{ij}\mathbf{n}_{ij}, \tag{16}$$

for liquid viscosity η_f and particle-particle unit vector $\mathbf{n}_{ij}$, where the squeeze resistances a_{sq} diverge with σ/h for particle-particle separation h, which is truncated at $h_{\min} = 0.001\sigma$ to prevent singularities. The contact force $\boldsymbol{F}_c$ is derived from an approximate square-well of width δ, for particle pairs separated by a distance r

$$\boldsymbol{F}_c = \begin{cases} k_1(\sigma - r) & \text{for } r \leq \sigma \\ 0 & \text{for } \sigma < r \leq (\sigma + \delta) \\ k_2[(\sigma + \delta) - r] & \text{for } (\sigma + \delta) < r \leq (\sigma + \delta + \xi) \\ 0 & \text{for } r > (\sigma + \delta + \xi) \end{cases} \tag{17}$$

where the outer attractive force is applied over a narrow region ξ chosen such that the cumulative force exerted upon entry into the well corresponds to the well depth Δ, which we set equal to $k_B T$. Random Brownian forces $\boldsymbol{F}_b$ are generated at each timestep according to Refs,[20,22] to satisfy $\langle \boldsymbol{F}_b \rangle = 0$ and $\langle \boldsymbol{F}_b(t)\boldsymbol{F}_b(t')\rangle = 2k_B T\boldsymbol{R}\delta(t - t')$. We simulate periodic domains with particle volume fractions of $\phi = 0.2$, 0.5 and 0.55, for two cases: one where

$\boldsymbol{F}_h$ is as described above, and the other where $\boldsymbol{F}_h = 0$ (and the Brownian force satisfies $\langle \boldsymbol{F}_b(t)\boldsymbol{F}_b(t')\rangle = 2k_BT(6\pi\eta_f r)\boldsymbol{I}\delta(t-t')^7)$.

For each case, we compute the system-averaged colloidal bond lifetime, i.e. the typical amount of time that a pair of particles spend with $r \leq (\sigma + \delta)$, as a function of the well width δ. We then compare the cases with and without hydrodynamic forces, presented in Fig. 4(a), as well as the effect of concentration ϕ, presented in Fig 4(b). For the lowest volume fraction considered, the lifetime measured in the simulation refers to colloidal dimers without many-body effects, whereas the latter become important upon approaching $\phi \approx 0.5$.
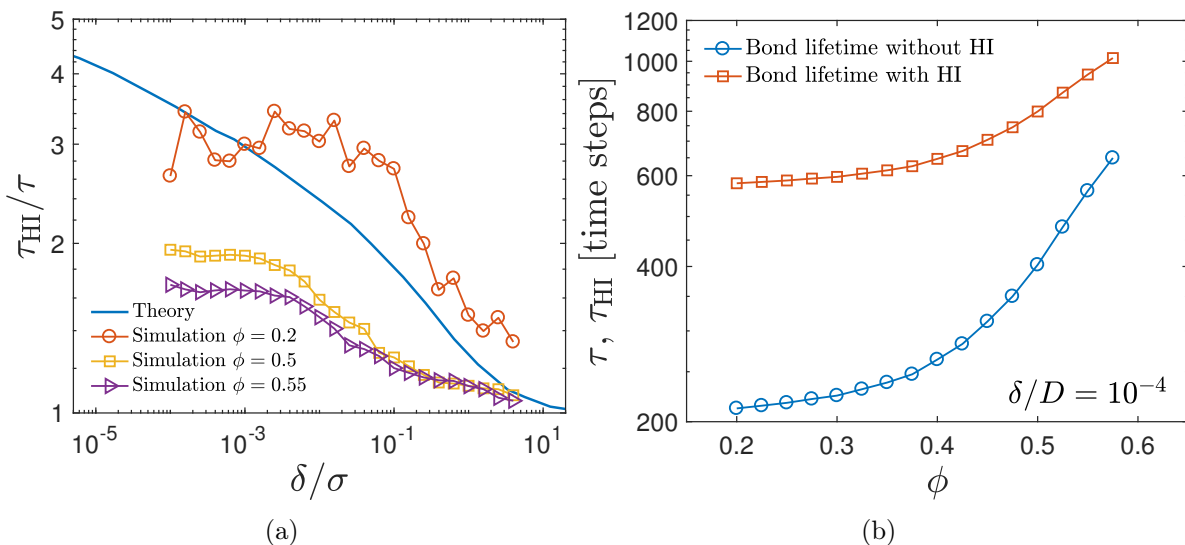

Figure 4: (a) The ratio between the colloidal bond lifetime with hydrodynamic interactions, τ_{HI}, and the lifetime without hydrodynamic interactions, τ. Shown are the theoretical result (solid line), and predictions from the simulation at three different volume fractions (symbols) as a function of δ/D. (b) Colloidal bond life-time versus concentration ϕ with and without hydrodynamic interactions, at $\delta/D = 10^{-4}$.

Comparison and discussion

Overall we find very satisfying agreement between the analytical theory and the simulation prediction, with the role of lubrication forces being most prevalent for short-range attractive

particles with small δ. For the lowest volume fraction considered, the agreement is excellent, in view of the simplifications used in the theory.

Moreover, we consider the role of many-body confinement as an additional contributor to bond lifetime for the more concentrated systems,[23] Fig 4(b). It is found that as the volume fraction is increased, the role of lubrication forces appears to diminish. This is particularly prevalent comparing $\phi = 0.2$ to $\phi = 0.5$ in Fig 4(a). This result has an intuitive physical explanation: as ϕ increases, the effects of confinement mean that particles are increasingly enclosed in cages by their neighbours, so that their motions become more localised and structural relaxation times are enhanced. Such an effect has previously been pointed out by Ref,[24] who found comparable dependence of bond life-time on volume fraction. Consistent with their reasoning, we might argue that as ϕ increases, bond life-times are increased due to steric and caging effects as the glassy regime is approached, which in general may be less sensitive to the presence or absence of lubrication forces. Further, recent numerical work[25] in dimerizing fluids found increasing association and decreasing self-diffusion rates with increasing ϕ, hinting at comparable volume fraction dependence across a broader class of systems. Unifying understanding of the influence of hydrodynamics on bond life-times across simple dimerizing and more fully percolating systems remains an outstanding challenge.

Finally, we shall briefly discuss the effect of the potential shape. Here we presented an analysis on the example of a square or rectangular well potential, because this is amenable to analytical manipulation and allows us to clearly single out the effect of the well width. Other types of attractive potentials that are frequently encountered in colloidal and soft matter systems are: the Lennard-Jones (LJ) potential with an attractive r^{-6} tail from the van der Waals attraction; the Yukawa-type potential $\sim e^{-r/\xi}/r$, where the range ξ is related to Debye-Hueckel screening of an attractive Coulomb potential; and the polymer depletion attraction in colloid-polymer mixtures where the range ξ of the attraction is dictated by the radius of gyration of the polymer which is depleted in the gap between two particles due to excluded-volume. In the case of the LJ potential, the effect that we described here

is expected to be very important: indeed, the inflection point of the LJ potential, beyond which the attractive force becomes much weaker, corresponds roughly to the same range $\delta/\sigma \approx 0.2 - 0.5$ where the effect of lubrication on the bond stability also becomes small. Clearly, this implies that the effect of hydrodynamic lubrication to stabilize the bonding is at least as important as the attractive force of the potential within the inflection point, and possibly more important. With LJ potentials a systematic study of the interplay between width and HIs similar to what we did here for the square well can be done in future studies by varying the power-exponent of the attractive part of the potential to values larger and smaller than 6. For the cases of Yukawa and depletion attraction, a similar effect is also expected to be found upon varying the size ξ of the Debye screening and of the polymer radius of gyration, respectively.

Conclusions and outlook

We have thus reported two key findings related to the role of lubrication forces on colloidal bond lifetimes, using the example of a square-well potential. First, the predicted colloidal bond lifetimes can be substantially increased, up to a factor 4, upon inclusion of lubrication forces; second, this effect is strongly modulated by the attraction range. This is evident for very narrow attractive wells where bonded particles experience diverging lubrication forces, which result in very long bond lifetimes. Conversely, if the range of the square well is sufficiently long (i.e. $> \sigma$, with σ being the particle diameter) the enhancement of the bond lifetime becomes negligible. The physical explanation for this strong effect lies in the reduced mutual diffusion coefficient due to lubrication forces. Since the mutual diffusion is the driving force for the particle to escape from the bond with a second particle, it is clear that reducing the diffusion must enhance the lifetime. We have shown here for the first time, using both analytical theory and numerical simulations, that this effect can be suppressed by taking longer-ranged attractions, because in that case the particles can explore regions

of the well where the diffusion coefficient is large enough (and close enough to its far-field value) to allow the Kramers escape process to take place.

We further showed that this effect of lubrication forces is less pronounced in systems that have higher volume fraction, where confinement plays an important role. The challenge remains to comprehensively link the constituent particle and fluid chemistry to the gel properties such as bonds lifetimes and mesoscopic percolation structures,[26] and then, ultimately, to form predictive theoretical links between these and the macroscopic rheological properties of the gel.[27–29] The single-bond lifetime, for which we provided a theory here, is also the starting point for a bottom-up description of the yielding of colloidal gels and glasses, and of the phenomenon of colloidal aggregate breakup under flow, where the escape is assisted by both diffusion and stress-transmission.[30–34] In a different context, the lifetime of colloidal bond may affect the kinetic evolution of clusters in colloidal nucleation, where a huge discrepancy persists between the nucleation rate from experiments (where HI are important) and from numerical simulations (where different approximations are used).[35,36]

In a more applied context, our results provide guidance for future approaches to strategic material design for gels and other colloidal and nano-structured materials. For example, one might tune the range of colloidal attraction to achieve appropriate bond lifetimes to form a synthetic gel with tailored stability, structure, and mechanical properties. Also, based on our finding, surface roughnesses may be tuned to decrease or enhance lubrication forces, with the effect of being able to control the bond lifetimes. Further applications of this present finding are in biological systems, where liquid films might play a mechanical role in enhancing contact duration while simultaneously playing a chemical role such as the transport of substrates between cells.

Finally, future work will be directed towards implementing depletion-attraction potentials in order to allow a quantitative comparison with recent experimental results by Furst and co-workers.[37] Another interesting direction would be to assess the effect of electrostatic repulsion and its interplay with both attraction and HI, which might introduce a different sensitivity

to HI altogether, and is important for a broad range of colloidal systems.[38,39]

Acknowledgement

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