# 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 the inclusion of lubrication forces, to an extent that depends on the attraction range. An analytical law is derived that 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 an increase in 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.
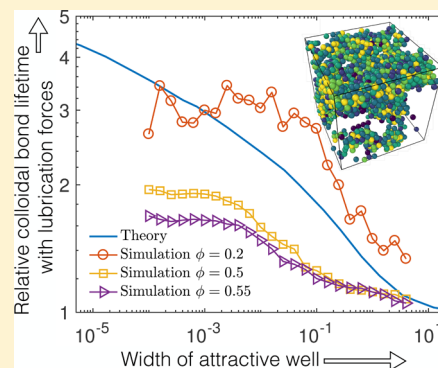
INTRODUCTION

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 because the particle–particle interactions may be precisely tuned by modifying the surface chemistry of, for example, poly(methyl methacrylate) (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 time scales 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_BT being sufficiently weak to break and reform under quiescent conditions. Further complicating this, though, is the

role of hydrodynamic interactions (HI) 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 HI can be important for large molecules and molecular complexes. In this area, a theory of the effect of HI 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 long-range hydrodynamics.

The importance of HI to gelation has now been appreciated,[9] and recent studies have attested to the augmenting role played specifically by long-range HI.[10,11] In the present study, we turn the attention to short-range HI (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 neighboring particles when lubrication forces are accounted for, which is crucially modulated by the attraction range. This interplay between

the 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 the 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 means that some neighboring 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, that is, $\phi = 0.50$ and 0.55, bond lifetimes are enhanced additionally by many-body confinement imposed by neighboring 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 $U =$ constant $= -\Delta$ 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 is the particle diameter (Figure 1).
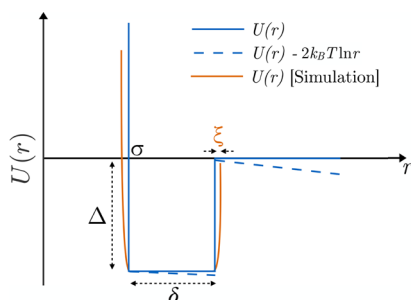

Figure 1. Attractive potential considered in this work. Shown are the square well $U(r)$, the square well adjusted for entropic effects $U_{\text{eff}}(r) = U(r) - 2k_BT \ln r$, and the simulation approximation.

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, $D_\infty = k_BT/(3\pi\mu\sigma/2)$ is 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 because of 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 because of the incompressibility of the solvent. Because the hydrodynamic interaction decays as $1/r$, the effect tends to vanish for a very long distance, where $D(r) \rightarrow D_\infty$ as $r \rightarrow \infty$.

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, because 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 Figure 2 and shows the expected trend.
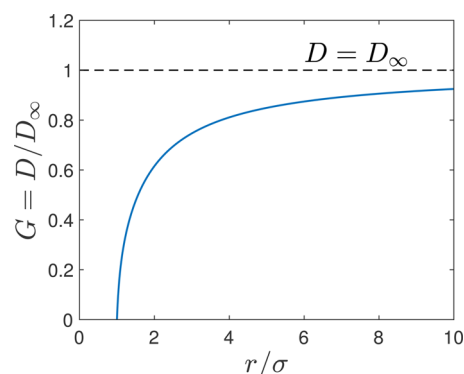

Figure 2. Lubrication correction to the Stokes−Einstein diffusion coefficient according to eq 1, which parametrizes the analytical solution of Stimson and Jeffery.

Here we show how the Kramers escape rate from such a square-well-bound state can be calculated upon accounting for two-body HI. 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 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 still applies. However, as we show below, this is not necessary because the integrals turn out to be exactly solvable for the square-well case.

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]

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

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 thermalized 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

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

The steady-state probability density in the well is given approximately by the stationary Boltzmann distribution $n(r) = n(r^*)\, e^{-[U(r)-U(r*)]/k_B T}$. 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 $\sigma + \delta$:

$$p = \int_{\sigma}^{\sigma+\delta} n(r)\, 4\pi r^2\, dr$$

$$p = n(r*)\, e^{U(r*)/k_B T} \int_{\sigma}^{\sigma+\delta} e^{-U(r)/k_B T} 4\pi r^2\, dr \tag{5}$$

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

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

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

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

This expression is exactly identical with the result that one would get in one dimension with a potential given approximately by the dashed line in Figure 1. Physically, this means that, in three dimensions, 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 one dimension, 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 following analytical expression for the rate of dissociation of a colloidal square-well bond in the presence of lubrication forces:

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

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

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

In the absence of HI, one has

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

and for the lifetime

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

The lifetime of a colloidal bond with HI, τ_{HI}, is compared with the lifetime in the absence of HI in Figure 3. It is evident
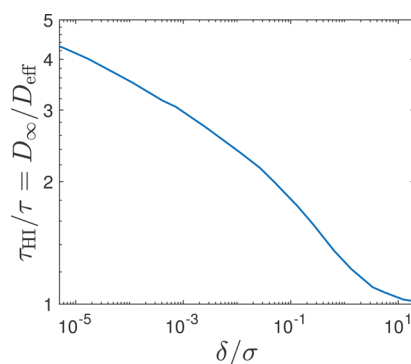

Figure 3. Ratio between the colloidal bond lifetime with HI, τ_{HI}, and the lifetime without HI, τ.

that with HI the lifetime of the colloidal bond is significantly larger than that 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 HI on the dissociation process, we introduce the following attraction-range-dependent (but r-independent!) effective diffusion coefficient for the dissociation process:

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

With this notation, the lifetime with HI can be written in terms of the lifetime without HI, where the Stokes−Einstein diffusivity is replaced by the effective one accounting for HI:

$$\tau_{HI} = \frac{2}{3} \frac{(\sigma+\delta)^3 - \delta^3}{\sigma(1+\delta/\sigma)D_{eff}} e^{\Delta/k_B T} = \tau D_\infty/D_{eff} \tag{13}$$
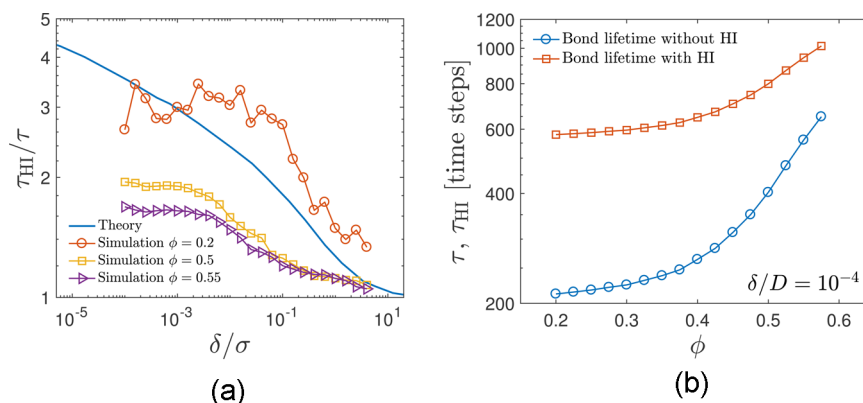
Figure 4. (a) Ratio between the colloidal bond lifetime with HI, τ_{HI}, and the lifetime without HI, τ. Shown are the theoretical result (solid line) and predictions from the simulation at three different volume fractions (symbols) as a function of δ/D. (b) Colloidal bond lifetime versus concentration ϕ with and without HI, at $\delta/D = 10^{-4}$.

and therefore

$$\tau_{HI}/\tau = D_\infty/D_{eff} \qquad (14)$$

The effect of two-body HI is to generate a stronger resistance to Brownian motion; hence, $D_{eff} < D_\infty$ always, and only in the far-field $r \rightarrow \infty$, one recovers $D_{eff} = D_\infty$ because the HI is long-range and vanishes at infinity. In the bond-breakup process, Brownian motion is the driving force that 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 of 4 for short-range attraction, by HI.

■ SIMULATION MODEL AND RESULTS

We solve the Langevin equation

$$m\frac{d\boldsymbol{v}}{dt} = \mathbf{F}_h + \mathbf{F}_c + \mathbf{F}_b \qquad (15)$$

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

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

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

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

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_BT. Random Brownian forces $\mathbf{F}_b$ are generated at each time step according to refs 20 and 22 to satisfy $\langle\mathbf{F}_b\rangle = 0$ and $\langle\mathbf{F}_b(t)\mathbf{F}_b(t')\rangle = 2k_BT\mathbf{R}\delta(t-t')$. We simulate periodic domains with particle volume fractions of $\phi = 0.2$, 0.5, and 0.55, for two cases: one where $\mathbf{F}_h$ is as described above and the other where $\mathbf{F}_h = 0$ (and the Brownian force satisfies $\langle\mathbf{F}_b(t)\mathbf{F}_b(t')\rangle = 2k_BT(6\pi\eta_f r)\mathbf{I}\delta(t-t')$[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 Figure 4a, as well as the effect of concentration ϕ, presented in Figure 4b. 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 $\phi \approx 0.5$.

■ COMPARISON AND DISCUSSION

Overall, we find very satisfying agreement between the analytical theory and 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 the bond lifetime for the more concentrated systems[23] (Figure 4b). It is found that, as the volume fraction is increased, the role of lubrication forces appears to diminish. This is particularly prevalent in the comparison of $\phi = 0.2$ and 0.5 in Figure 4a. This result has an intuitive physical explanation: as ϕ increases, the effects of confinement mean that particles are increasingly enclosed in cages by their neighbors, so that their motions become more

localized and structural relaxation times are enhanced. Such an effect has previously been pointed out in ref 24, in which a comparable dependence of the bond lifetime on the volume fraction is found. Consistent with their reasoning, we might argue that, as ϕ increases, bond lifetimes are increased because of 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 a comparable volume fraction dependence across a broader class of systems. A unified understanding of the influence of hydrodynamics on the bond lifetimes 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 of 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 a Debye−Hückel 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 the width and HI 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 of 4, upon the 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. Because 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 a 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 bond 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 the 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 nanostructured 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, on the basis of 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 the contact duration while simultaneously playing a chemical role such as the transport of substrates between cells.

Finally, future work will be directed toward implementing depletion−attraction potentials in order to allow a quantitative comparison with recent experimental results by Whitaker and Furst.[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]

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Notes
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