

Simple models for two-dimensional tunable colloidal crystals in rotating ac electric fields

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We compare the behavior of a new two-dimensional aqueous colloidal model system with a simple numerical treatment. To the first order the attractive interaction between the colloids induced by an in-plane rotating ac electric field is dipolar, while the charge stabilization leads to a shorter ranged, Yukawa-like repulsion. In the crystal-like “rafts” formed at sufficient field strengths, we find quantitative agreement between experiment and Monte Carlo simulation, except in the case of strongly interacting systems, where the well depth of the effective potential exceeds 250 times the thermal energy. The “lattice constant” of the crystal-like raft is located approximately at the minimum of the effective potential, resulting from the sum of the Yukawa and dipolar interactions. The experimental system has display applications, owing to the possibility of tuning the lattice spacing with the external electric field. Limitations in the applied field strength and relative range of the electrostatic interactions of the particles result in a reduction in tunable lattice spacing for small and large particles, respectively. The optimal particle size for maximizing the lattice spacing tunability was found to be around 1000 nm. © 2009 American Institute of Physics.

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I. INTRODUCTION

Colloidal suspensions present the possibility to develop novel materials via self-assembly. Of particular interest are colloidal crystals, whose optical properties can generate iridescent colors and provide a means by which photonic crystals may be produced,¹ while further applications range from lasers² to display devices,³ with recent advances demonstrating tunable colors through control of lattice spacing with an external field.⁴ Further to the practical importance of colloidal crystals, their well-defined thermodynamic temperature allows colloidal dispersions to be viewed as mesoscopic “model atoms.”⁵

Recently, the ability to tune the colloid-colloid interactions led to the observation of a wide variety of structures.^{6–11} Of particular interest here, to the first order ac electric fields can induce dipolar interactions between the colloidal particles, leading to anisotropic interparticle potentials and exotic crystal structures, some of which are not observed in atomic and molecular systems,⁷ while external control of the colloid-colloid interactions allows direct observation of phase transitions.¹² Furthermore, direct microscopic observation at the single-particle level allows an unprecedented level of detail to be accessed,¹³ opening the possibility of tackling long-standing problems in condensed matter, such as freezing.¹⁴

The introduction of a rotating ac field opens up even more possibilities. In this case, the dipolar interactions lead to attraction in the plane of rotation and to repulsions above

and below. Studies with a rotating magnetic field on granular matter indeed produced disklike patterns consistent with expectations.^{15,16} Unlike granular matter, since colloidal dispersions exhibit Brownian motion, thermodynamic equilibrium structures (i.e., crystals) may be obtained.^{11,17} In a previous work Snoswell *et al.*¹¹ showed that lattice spacing within quasi-two-dimensional (quasi-2D) colloidal crystals could be controlled *in situ*, by means of coplanar rotating electric field. The interparticle dipolar interactions in the plane of the electric field may be treated to first order as a circularly symmetric attraction, due to the time averaging effect of a rapidly rotating field (1000 Hz) on relatively large particles on the micron lengthscale, where the diffusive timescale is of the order of seconds.¹⁸

In considering the interactions between particles, the asymmetry between the colloids (10 nm–1 μ m) and smaller molecular and ionic species must be addressed. A number of coarse-graining schemes have been developed where the smaller components are formally integrated out.¹⁹ This generates a one-component picture, where only the effective colloid-colloid interactions are considered, and the complexity of the description is vastly reduced. The equilibrium behavior of the colloids in the original multicomponent system may then be faithfully reproduced by appeal to liquid state theory²⁰ and computer simulation.²¹ Central to the success of this one-component approach is the use of a suitable effective colloid-colloid interaction $u(r)$.

In this study, we use a simple numerical treatment in which we can predict the lattice spacing in the quasi-2D crystal from the electric field strength. We consider a model system of charged colloids in a rotating electric field.¹¹ By

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TABLE I. Fitted parameters of the Debye screening length used in the MC simulations for systems with different colloid diameters. Errors in the diameter are standard deviations in the data obtained found from electron microscopy measurements, while those in $\beta\epsilon$, $\kappa\sigma$, and the ionic strength are estimated from the fitting of d from MC data. ζ potential measurements were made in a 0.01 mmol KCl solution.

Diameter (nm)	Effective Yukawa contact potential $\beta\epsilon$	$\kappa\sigma$	Ionic strength (mmol)	ζ potential (mV)	Melting well depth ($k_B T$)
757 ± 86	$4.60 \pm 0.05 \times 10^3$	19.0 ± 1.0	0.06 ± 0.01	-34.0 ± 1.4	2.7 ± 0.1
965 ± 44	$5.78 \pm 0.02 \times 10^3$	28.4 ± 2.0	0.08 ± 0.01	-37.1 ± 1.4	2.9 ± 0.1
1390 ± 30	$8.27 \pm 0.05 \times 10^3$	32.3 ± 3.0	0.05 ± 0.005	-39.9 ± 2.0	3.1 ± 0.1
2070 ± 40	$1.17 \pm 0.01 \times 10^4$	38.8 ± 3.0	0.04 ± 0.005	-43.6 ± 2.4	3.4 ± 0.1

exploiting the knowledge both of the electrostatic repulsions and dipolar attractions, we present a direct, quantitative comparison of a tunable interaction and a material property of the crystalline “rafts” formed. We combine experimental measurements of the crystal lattice constant d as a function of field strength E with Monte Carlo (MC) simulations according to a screened Coulomb repulsion plus dipolar attraction where the only fitting parameter is the Debye screening length.

In the simulations, we used pairwise interactions, in other words, we assumed that at the higher densities at which the crystalline rafts are formed, the system is still accurately described by interactions calculated for two particles in isolation. We note that deviations from this assumption of pairwise additivity have been measured both in the case of strongly charged colloids²² and in the case of *repulsive* dipolar interactions.²³ We further compare simulation results with the minimum of the effective potential, which we take as a measure of the lattice constant of the crystalline rafts, which we also determine from experimental data.

This paper is organized into six sections. In Sec. II we present expressions for the effective interactions between the colloids, summing the attractions and repulsions to provide an effective one-component description of the system. Section III describes our experimental methodology. Section IV outlines the MC simulation technique employed. The comparison of simulation and experimental results is presented in Sec. V and in Sec. VI we extrapolate our findings to maximize the tunability of the crystal lattice constant, which may be useful for applications. We conclude our findings in Sec. VII.

II. THEORY AND MODEL

In the following we will consider a system consisting of two particles in a surrounding medium. We shall assume that these particles are charged, leading to a repulsive interaction, and that the rotating ac electric field induces a dipole moment in the two particles and thus induces an attractive interaction. To describe this system, we start from the Derjaguin, Landau, Verwey, and Overbeek (DLVO) approach,²⁴ which consists of attractive van der Waals interactions at short range and long-ranged repulsive electrostatic interactions. The van der Waals interactions are very short-ranged and are neglected, as electrostatic repulsions inhibit the close approach at which van der Waals interactions become impor-

tant. We shall therefore assume that the only relevant attractions result from the long-ranged dipolar interactions induced by the rotating electric field.

In the linear Poisson–Boltzmann regime, the electrostatic repulsions may be expressed as a hard core Yukawa or screened Coulomb interaction,²⁴

$$\beta u_{\text{yuk}}(r) = \begin{cases} \infty & \text{for } r < \sigma \\ \beta \epsilon_{\text{yuk}} \frac{\exp(-\kappa(r-\sigma))}{r/\sigma} & \text{for } r \geq \sigma, \end{cases} \quad (1)$$

where $\beta = 1/k_B T$, where k_B is Boltzmann’s constant, T is temperature and σ is the colloid diameter. The potential at contact $\beta \epsilon_{\text{yuk}}$ is given by

$$\beta \epsilon_{\text{yuk}} = \frac{Z^2}{(1 + \kappa\sigma/2)^2} \frac{l_B}{\sigma}, \quad (2)$$

where Z is the colloid charge, l_B is the Bjerrum length, and $\kappa = \sqrt{4\pi l_B \rho_i}$ is the inverse Debye screening length where ρ_i is the total number density of monovalent ions.

Now the regime of the linear Poisson–Boltzmann theory in which Eq. (1) holds corresponds to relatively weak charging. Although this is not the case here, a potential of the Yukawa form is recovered at larger separations, if a smaller, renormalized charge is considered.²⁵ We tabulate measurements of the ζ -potential of dilute suspensions in Table I. These values suggest that we expect a renormalized charge in the conditions under which the colloids form the crystalline rafts, rather high colloid concentration, hence high counter ion concentration.^{18,25} Therefore, noting that the Debye length is much smaller than the colloid radius, we follow Bocquet *et al.*²⁶ and take the following expression for the renormalized charge Z_{eff} :

$$Z_{\text{eff}} = \frac{4\sigma(1 + \kappa\sigma/2)^2}{l_B(1 + \kappa\sigma)}, \quad (3)$$

which we substitute for Z in Eq. (2). This expression gives good agreement with measurements of the effective colloid charge for particles with a comparable ζ -potential.²⁷ We recall that many-body effects can lead to a density dependence in the effective colloid-colloid interactions.^{22,23} However, we shall neglect these effects in the present work.

The attractive potential between the colloids resulting from the rotating ac electric field is treated to first order as a dipolar interaction,

$$u_{\text{dip}}(r) = \frac{(p \times p)}{2\pi\epsilon\epsilon_0 r^3}, \quad (4)$$

where p is the induced dipole moment of each particle, ϵ is the dielectric constant, and ϵ_0 is the permittivity of free space. The dipole moment may be calculated from the strength of the electric field,

$$p = \frac{1}{2}\pi\epsilon\epsilon_0\sigma^3 KE, \quad (5)$$

where K is the Clausius–Mosotti factor and takes values between 1 and $-1/2$ depending on the origin of the dipole moment. We note that in this case of an alternating field, the root-mean-square of the time dependent field is taken. Substituting $r = \sigma$ leads us to a potential at contact

$$\epsilon_{\text{dip}}(\sigma) = \frac{(p \times p)}{2\pi\epsilon\epsilon_0\sigma^3}, \quad (6)$$

which has a cubic dependence on the colloid diameter, in the case of all other contributions being unchanged.

In considering the value of the Clausius–Mosotti factor, two regimes are relevant, corresponding to applied electric fields of high and low frequencies, in which the dipolar interactions result from dielectric permittivity differences between the particles and the solvent and differences in conductivity, respectively.⁶ The crossover frequency ω^* between these regimes is given by

$$\omega^* = \frac{1}{2\pi\epsilon_0} \sqrt{-\frac{s_p^2 - 2s_p s_m + 2s_m^2}{\epsilon_p^2 - \epsilon_p \epsilon_m + 2\epsilon_m^2}}, \quad (7)$$

where s are conductivities and the indices p and m refer to the colloidal particles and the medium, respectively. Following Ref. 28 the conductivity of the particles s_p is taken to be the sum of the bulk conductivity $s_b \approx 0$ and the conductivity on the surface s_s ,

$$s_p = s_b + s_s \sigma. \quad (8)$$

In principle Eq. (8) holds for particles larger than $1 \mu\text{m}$. In the case of much smaller particles, one should take into account that the contribution of the diffuse layer to the conductivity of the particles. Noting that the smallest particles used in the experiments are 757 nm in diameter and that the conductivity of the de-ionized water is relatively low, we neglect the double layer contribution and thus use Eq. (8). Since the largest particles studied are 2070 nm in diameter, the frequency is 1 kHz, and the bulk ionic strength is 0.01–0.1 mmol as determined from conductivity measurements, we work in the low frequency regime where the contributions from the conductivities dominate.²⁸ The Clausius–Mosotti factor therefore takes the following form:

$$K_s = \frac{s_p - s_m}{s_p - 2s_m}. \quad (9)$$

Due to the surface conductivity, s_p is much larger than the conductivity of the medium s_b . The value of K_s is therefore close to one. We now combine the contributions from the electrostatic repulsions and the dipolar attractions, yielding the expression

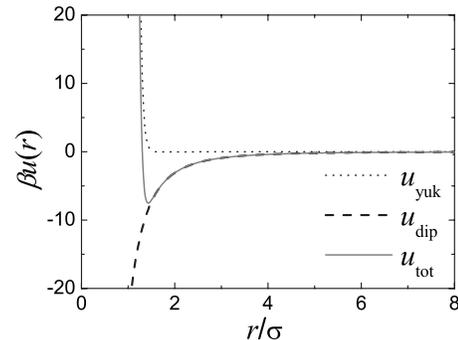


FIG. 1. The interaction potentials considered in this system. The Yukawa repulsion $u_{\text{yuk}}(r)$ models the electrostatic repulsions [dotted line, Eq. (1)] and the dipolar attractions are plotted as $u_{\text{dip}}(r)$ dashed line, [Eq. (4)]. These are combined to yield the total potential $u_{\text{tot}}(r)$, solid gray line [Eq. (10)]. This figure corresponds to a particle diameter of $\sigma = 757 \text{ nm}$ and a field strength $E = 30 \text{ kV m}^{-1}$

$$u_{\text{tot}}(r) = u_{\text{yuk}}(r) + u_{\text{dip}}(r). \quad (10)$$

u_{tot} has the form indicated in Fig. 1. We see a minimum in the potential, which one might expect to provide a first approximation to the lattice constant in the 2D colloidal crystal. In Secs. V and VI we shall compare this minimum to our simulation results.

III. EXPERIMENTAL

Colloidal crystals underwent self-assembly as a result of an applied electric field. We used anionic, sulfate stabilized polystyrene latex particles, either synthesized using a standard technique, surfactant free emulsion polymerization²⁹ in the case of $\sigma = 757$ and 945 nm, or particles produced by the same method but purchased from Microparticles GmbH for $\sigma = 1390$ and 2070 nm.

Particle electrophoretic mobility was measured using a Brookhaven Zetaplus light scattering instrument. Particle sizes were determined by scanning electron microscopy, either in-house using a Jeol JSM-6330F, in the case of $\sigma = 757$ and 945 nm or by Microparticles GmbH for $\sigma = 1390$ and 2070 nm are listed in Table I. Experiments were performed with dilute aqueous suspensions (0.5–1.5 wt %). Schematics of the experimental setup are shown in Fig. 2. All glass surfaces were chemically washed with 0.1M KOH and washed with copious quantities of MilliQ water. Particles were deionized by direct contact with ion exchange beads before being made up to the desired electrolyte concentration with KCl. Very low salt conditions are required as even moderate (mmol) salt concentrations lead to electrohydrodynamic pattern formation due to ion flow.^{30,31} For further details on the experimental setup and procedure the reader is referred to Snoswell *et al.*¹¹

We consider our experiment as a 2D system. However, occasionally we notice some overlap on the crystalline rafts. We do not include these results in our analysis. In order to treat the system in 2D, one might expect the gravitational length $l_g = k_B T / mg$, where m is the bouyant mass of the particle and g is the acceleration due to gravity, to be much less than some characteristic length such as the particle diameter. Due to the fairly small density mismatch between polysty-

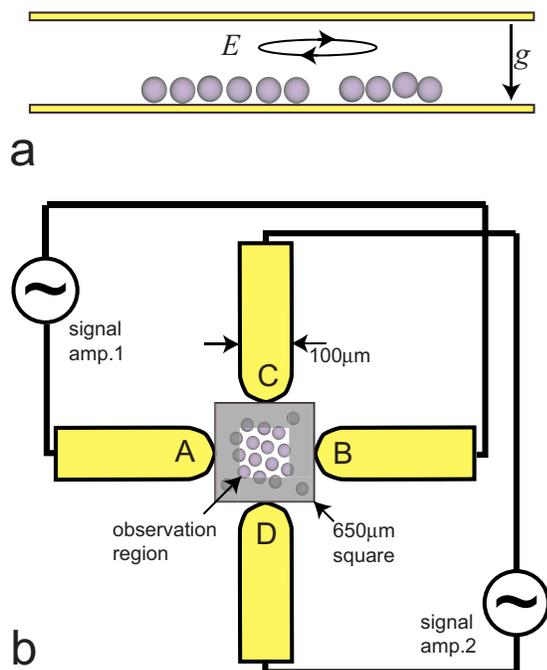


FIG. 2. (Color online) A schematic of the experimental setup, (a) side view and (b) plan view. The electric field is assumed to be constant across the observation region, as shown in (b). (b) depicts the quadrupolar electrode configuration [(a),(b)], [(c),(d)].

rene and water, in fact even for the largest particles $\sigma = 2070$ nm, $l_g \approx 0.87\sigma$. However, the dipolar interactions between the particles are attractive in-plane, but strongly repulsive in the vertical direction. This promotes the formation of rafts and “sheets,” and these large assemblies of many particles have very small gravitational lengths. Thus we argue that the system behaves in a quasi-2D manner. The lattice parameter d was taken as the average of typically ten crystalline rafts, measured across the raft, of around ten lattice spacings. The response to changing the electric field strength was determined to be less than 100 ms, we waited 5s after changing the field strength before acquiring data.

IV. MONTE CARLO SIMULATION

We use standard MC simulations in the NVT ensemble.²¹ The particles interact via Eq. (10) in two dimensions. To mimic the experiments, we initialize the system in a random configuration at a relatively low concentration, corresponding to an area fraction $\phi = 0.05 - 0.3$. We confirmed that different area fractions gave indistinguishable results, however, smaller area fractions often led to longer equilibration times. The attractive interactions cause the particles to approach one another and form crystallites, which then coalesce to form crystalline rafts, which contain of order of 100 particles, in a qualitatively similar way to the experimental system. Each simulation was equilibrated for typically 30 000 MC moves per particle, followed by 3000 production moves per particle. We recall that a potential of the form $1/r^3$ converges in 2D. The lattice constant for this 2D hexagonal crystal was taken as

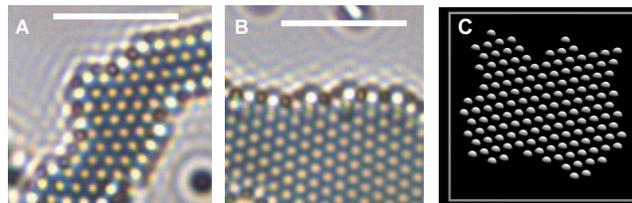


FIG. 3. (Color online) Images of crystal rafts for the $\sigma = 945$ nm system for applied fields of 29.0 and 80.0 kV m^{-1} for (a) and (b), respectively. Scale bars = 10 μm . (c) snapshot from MC simulation for same system for a field of 30.0 kV m^{-1} and $N = 144$.

$$d = \frac{\int_0^b r g(r) dr}{\int_0^b g(r) dr}, \quad (11)$$

where $g(r)$ is the pair correlation function and b is the minimum between the first and second peaks of $g(r)$.

We found that, when we used $N < 200$, typically one crystalline domain was formed around the center of the simulation box. We therefore do not use periodic boundary conditions and consider the lattice spacing of the single crystal formed in the simulation. One parameter is the number of particles typically present in each crystalline domain. This is estimated to be around $N = 100 \pm 25$ from experimental data (see Fig. 3). This value is governed by the overall concentration of the colloidal suspension. We considered the effects of varying N as shown in Fig. 4. The results of a considerable range of N resulted in a variation of d around one percent in d for the $\sigma = 945$ nm system for a field $E = 20$ kV m^{-1} . Each simulation was repeated four times except $N = 576$. We found a slight trend to tighter binding for larger N , however, as shown in Fig. 4; this effect is rather small. We henceforth use one simulation per state point unless otherwise stated. The slight scatter in the simulation data is perhaps indicative the existence of different “magic numbers” for these crystalline rafts.³² These may be thought of as 2D hexagonal clusters, whose magic numbers, i.e., low energy states, are expected to include 7, 19, 37, ... Close to a magic number the binding may be expected to be relatively tighter. A more detailed exploration of this phenomenon lies beyond the scope of this work. Overall, the variation in d as a function of N is smaller than the experimental scatter, nonetheless, we take both $N = 72$ and $N = 144$ values for d

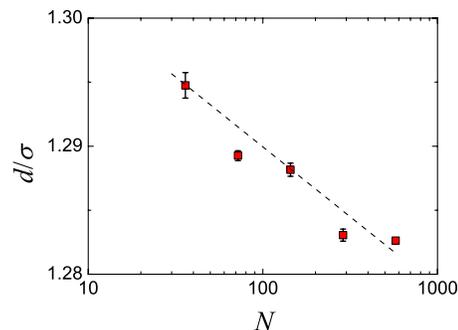


FIG. 4. (Color online) Change in the lattice constant for simulated systems of different sizes. Here $\sigma = 945$ nm and a field strength $E = 20$ kV m^{-1} . Each run was repeated four times except $N = 576$. Error bars denote standard deviations over the results from different runs. Dashed line is solely a guide to the eyes.

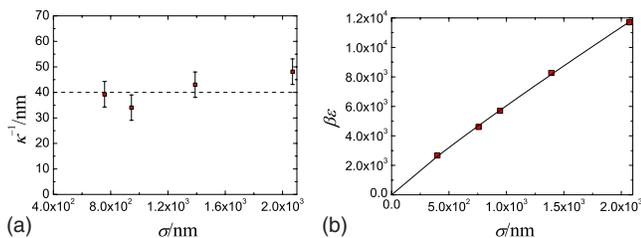


FIG. 5. (Color online) (a) The Debye length κ^{-1} fitted from MC simulation as a function of particle size. Dotted line denotes $\kappa^{-1}=40$ nm taken for the simulations in Sec. VI. Error bars denote the uncertainty in the Debye length resulting from the fitting in Figs. 7 and 8. (b) The contact potential of the Yukawa interaction $\beta\epsilon_{\text{yuk}}$ [Eq. (2)] as a function of particle size. We include $\sigma=400$ nm for which we take the Debye length $\kappa^{-1}=40$ nm. The straight line is fit of the function $\beta\epsilon_{\text{yuk}}(\sigma)=A\sigma^b$, where the fitted parameters are $A=11.1 \pm 1.1$ and $b=0.91 \pm 0.01$.

when comparing with experimental data. The slightly larger value for $N=32$ in Fig. 4 is attributed to the small size of the crystalline raft, such that the surface particles which are more widely spaced make a greater contribution. The domain size is of the order of 100 particles, thus, for larger N , defects and grain boundaries may lead to a smaller contribution to the measurement of d . This also applies to the experimental data.

For fitting, all parameters are known, except the Debye length κ^{-1} , which we take as a free parameter for each particle size and salt concentration, although we note that the effective colloid charge is itself a function of the Debye length, Eq. (3). It has previously been shown that comparison of simulation and experimental data can yield a reasonable *local* measure of the Debye length.³³ Furthermore, in the region of the sample in which the electric field is applied, the colloid volume fraction is much higher, and due to the colloidal counter ions the ionic strength may increase, leading to a reduction in the Debye length with respect to the bulk. However, it is the Debye length in this region which is relevant for the effective colloid-colloid interactions. The bulk Debye length that may be determined, for example, from conductivity measurements, may therefore be taken only as an upper bound. System parameters for different particle sizes are tabulated in Table I and the Debye length is plotted in Fig. 5(a); the contact potential of the Yukawa interaction [Eq. (2)] in Fig. 5(b) are plotted as a function of particle diameter.

Clearly, our MC simulations may be expected to provide a reasonable treatment of the crystalline rafts in (quasi-) equilibrium, rather than to describe the formation process. We therefore restrict our analysis to a simple characterization of the crystal rafts and primarily consider lattice spacing. We furthermore note both here and in a previous work¹¹ that considerable variation in shapes of crystalline rafts was observed, but that this had little impact on the measurement of the lattice spacing d . Likewise, at the level of this work, we neglect possible local variations in d due to the proximity of an interface. In any case we note that for display applications, all lattice spacings contribute to the diffraction. A few words on equilibration are in order. This applies both to the experimental system and to the simulations. Neither system is strictly in equilibrium; in that case we might expect a rather regularly shaped raft such as a hexagon. However, the

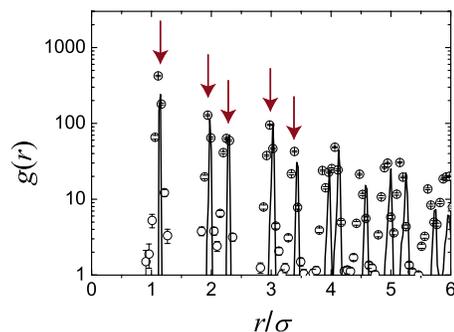


FIG. 6. (Color online) Radial distribution functions for an applied field of $E=30.7$ kV m $^{-1}$ for the $\sigma=2070$ nm system. Circles are experimental data and the line is MC simulation for $N=144$. Arrows denote the first few peaks of a hexagonal lattice, $d, \sqrt{3}d, 2d, \sqrt{7}d, 3d, \dots$.

insensitivity of the lattice parameter either as a function of N (Fig. 4) and the very close agreement between statistically independent simulation runs lead us to conclude that our approach is sufficient to compare lattice parameters between experiment and simulation.

V. RESULTS

The effect of changing the electric field strength is readily demonstrated in Fig. 3, which shows optical microscope images of the region of the sample in which the field is applied. Two field strengths are shown, (a) 29 kV m $^{-1}$ and (b) 80 kV m $^{-1}$ for $\sigma=945$ nm and we see a correspondingly tighter lattice in the case of the higher field strength. Similar behavior was observed in Ref. 11. Figure 3(c) illustrates simulated coordinates for $\epsilon_{\text{yuk}}=5.78 \times 10^3 k_B T$, $\kappa\sigma=28.4$, and $\epsilon_{\text{dip}}=50.1 k_B T$, which corresponds to $E=29.0$ V m $^{-1}$ for the $\sigma=945$ nm system (see Table I).

A more quantitative comparison between experiment and simulation is shown in Fig. 6, which plots the radial distribution function $g(r)$. We see that the structure appears to be crystalline, with reasonably long-ranged correlations, although, as is clear from Fig. 3, the system is too small to test for truly long-ranged order. We thus note that it is difficult to distinguish the true crystal from a hexatic phase in this system. However, our motivation is to model the experimental system, with $N=100 \pm 25$ and thus we argue that identification of the hexatic phase lies beyond the scope of this work.

Having illustrated the general behavior of the system, we now turn our attention to the fitting of the experimental data, with the model described in Sec. II. The experimental data was fitted to the theory by taking the Debye length as the fitting parameter.

The main results are shown in Figs. 7 and 8 for $\sigma=757$ and 945 nm, and $\sigma=1390$ and 2070 nm systems respectively. These concern the lattice parameter d as a function of applied field strength E . In general, the simulation is able to capture the behavior of the system in a reasonably quantitative manner. Furthermore, simply plotting the minimum in the potential u_{min} given by Eq. (10) provides a first approximation to the lattice constant d . Figure 7(a) shows the results for $\sigma=757$ nm particles. Due to the small particle size and the inverse cubic dependence of the strength of the dipolar attractions on the particle diameter, as characterized

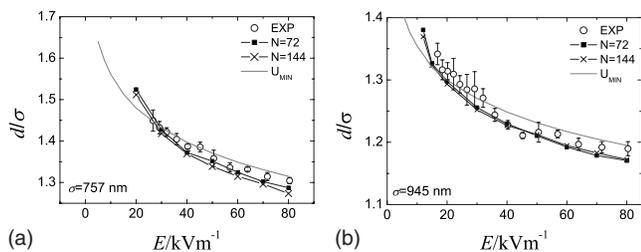


FIG. 7. Experimental results compared to MC simulation and the minimum in the effective potential. (a) 757 and (b) 945 nm diameter colloids. Filled squares are $N=72$ while crossed are $N=144$ from MC simulation. Circles are experimental data. Grey lines are the minimum of Eq. (10). Error bars in the experimental data are standard deviations.

by ϵ_{dip} [Eq. (6)], the attraction for a given field strength is comparatively small, so we find relatively larger lattice parameters for this system. At low field strengths ($E < 20 \text{ kV m}^{-1}$) we see an increase in the lattice constant for both the experimental data and the simulation, compared to the minimum in the potential. Apparently, as the crystal approaches melting, fluctuations become more pronounced, leading to an increase in d , which is not captured in Eq. (10), or perhaps a molten surface layer increases the apparent value of d . We leave this intriguing question for further investigations. Meanwhile, at high field strengths, we find some deviation between simulation, experiment, and Eq. (10). Apparently, due to the long ranged nature of the interaction, second nearest neighbors experience an attraction of sufficient strength that the crystal is compressed by its own cohesion, leading to a smaller lattice constant.

In the case of the $\sigma=757 \text{ nm}$ particles, we find that for small field strengths, ($E=10 \text{ kV m}^{-1}$), the system does not form crystallites, rather it remains as a colloidal liquid. We determined this both by experimental observation and with simulations. In the latter case, we identified crystallization with a splitting in the second peak of the pair correlation function $g(r)$. The kink around $E \sim 20 \text{ kV m}^{-1}$ in Fig. 7 is likely related an artifact of measuring multiple rafts, so defects and grain boundaries contribute to the value of d . At weak field strengths the rafts tend to be smaller, thus increasing this effect.

At larger particle sizes, (Fig. 8) we again see reasonable agreement between experiment and simulation, albeit with some deviation between simulation and Eq. (10) at higher field strengths, as the simulation predicts a smaller lattice constant than that observed in the experiments. However, for

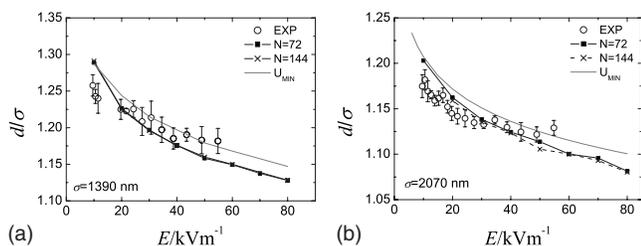


FIG. 8. Experimental results compared to MC simulation and the minimum in the effective potential. (a) 1390 and (b) 2070 nm diameter colloids. Filled squares are $N=72$ while crossed are $N=144$ from MC simulation. Circles are experimental data. Gray lines are the minimum of Eq. (10). Error bars in the experimental data are standard deviations.

the $\sigma=1390 \text{ nm}$ system, in particular, in fact Eq. (10) provides a more accurate description of the experimental data. Apparently some of our assumptions in the simulations, perhaps that of pairwise additivity, begin to break down at high field strengths. According to Eq. (10), the potential at the minimum of the attractive well is some $250k_B T$ for an applied field of 50 kV m^{-1} for $\sigma=1390 \text{ nm}$. Thus we conclude that for moderate interaction strengths, Eq. (10) provides a reasonable description of the system.

We now consider the dependence of the system upon the colloid diameter σ . First, we see from Fig. 5(a) that the absolute value of the (fitted) Debye length κ^{-1} does not change significantly for all the four particle sizes studied. Thus, the reduced inverse Debye length $\kappa\sigma$ is linear in σ . The contact potential $\beta\epsilon_{\text{yuk}}$ has an approximately inverse cubic dependence on σ for $\kappa\sigma \gg 1$, Eq. (2), but also depends on the (effective) charge Z_{eff} . Plotting $\beta\epsilon_{\text{yuk}}$ as a function of σ in Fig. 5(b) we find an approximate power law dependence with an exponent of $b=0.91 \pm 0.01$.

As noted above, the prefactor of the dipolar attraction, ϵ_{dip} [Eq. (6)], has σ^{-3} dependence. Although the electrostatic interactions are non-negligible, we nonetheless expect from Eq. (6) that upon decreasing σ we find a relatively larger lattice constant for a given field strength, and that larger field strengths are required to provide sufficient interactions that the crystalline rafts form. This we indeed find, as shown in Figs. 7 and 8, and also in the next section.

VI. OPTIMIZING THE TUNABILITY

Now we note that this system has optical display applications, due to the possibility of externally tuning the lattice parameter d . These applications may be most usefully realized when the possibility to tune the system is maximized, i.e., when the range of d is maximized. We are therefore motivated to consider a range of particle sizes and calculate the range of tunability of d . Now σ sets a lower bound to d while the upper bound is set by the melting transition, which can be determined by MC simulation.

Hitherto, we used the Debye length κ^{-1} as a fitting parameter. However, as Fig. 5(a) shows, there is relatively little change in the absolute value of the Debye length for the range of colloid diameters investigated. We therefore fix $\kappa^{-1}=40 \text{ nm}$ and vary the colloid size, and apply the same methodology as that outlined in Secs. II and IV in calculating the response for $\sigma=400\text{--}2000 \text{ nm}$ colloids to an external electric field. While an accurate determination of the melting transition is complicated by the small system size, melting is approximately determined by the splitting of the second peak in the radial distribution function $g(r)$.³⁴ We decrease the electric field to identify the weakest field at which the second peak in $g(r)$ exhibits clear splitting [Fig. 9(a), inset], thus yielding $d(E_{\text{min}})$, the lattice spacing just prior to melting. The melting value of the lattice parameter d_m is taken as

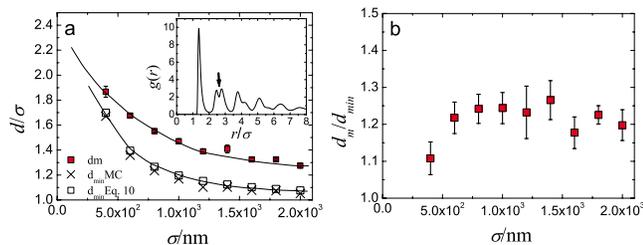


FIG. 9. (Color online) (a) The lattice spacing around melting (d_m , filled squares) and at applied field of 100 kV m^{-1} , as determined from MC simulation (crosses) and from Eq. (10), as a function of particle size. The inset shows a radial distribution function close to melting ($\sigma = 1000 \text{ nm}$, $E = 11.0 \text{ kV m}^{-1}$). The arrow indicates split second peak. (b) The tunability ratio as a function of particle size. Connecting lines are guides to the eyes.

$$d_m = d(E_{\min}) + \frac{d(E_{\min} + \delta E)}{2}, \quad (12)$$

where δE is the amount by which the field strength is varied between simulations, typically $0.5\text{--}1.0 \text{ kV m}^{-1}$. The error in d_m is then taken as $d_m - d(E_{\min})$.

In terms of the particle diameter, d_m grows considerably at small sizes, as the relatively larger Debye length leads to a minimum in the effective potential at relatively larger distances. However, we recall that our analysis suggests a roughly σ^3 dependence of ϵ_{dip} the strength of the dipolar attraction. This suggests that we might expect a stronger electric field to be required for relatively small colloids and indeed we find that a higher field is required to provide sufficient cohesive energy to hold the colloids together in the crystal-like rafts, so at 100 kV m^{-1} , a value we take as a reasonably accessible maximum field strength, the lattice spacing is still around $d_{100} \approx 1.6\sigma$ for $\sigma = 400 \text{ nm}$, where d_{100} is the lattice spacing corresponding to a field strength of 100 kV m^{-1} . Conversely, at larger particle sizes, the Debye length is relatively small, so we find, even at melting, that the lattice constant only approaches around 1.2σ . We note that, at high field strengths, the assumptions of Sec. II will ultimately break down. The results presented in Figs. 7 and 8 show that $E < 100 \text{ kV m}^{-1}$ is reasonable, at least for $\sigma > 757 \text{ nm}$, supporting our conclusion of a maximum in tunability around 1.2σ . We show the values of the well depth of Eq. (10) at melting for the different experimental systems in Table I, which indicates a trend toward deeper wells for larger particles, i.e., shorter ranges of the repulsive interaction relative to the particle size.

Larger field strengths may be expected to yield greater tunability for the small particle sizes. Since the overall minimum lattice spacing is $d = \sigma$, in principle smaller particles have greater tunability, however experimental observations reveal intense fluid turbulence disrupts crystal formation at higher field strengths. This is caused by large field gradients at the electrode edges that induce strong dielectrophoretic forces. In addition, higher field strengths can cause bubble formation by electrolysis and electrochemical degradation of the electrodes.

The result is thus that intermediate particle sizes have the highest degree of tunability for a given maximum field

strength. Here we considered 100 kV m^{-1} , which leads to a maximum tunability of d_m/d_{100} in the range of $1000 \text{ nm} < \sigma < 1500 \text{ nm}$.

VII. CONCLUSIONS

2D colloidal crystalline rafts with externally controllable properties have been modeled with MC simulations and the resulting lattice constant, both experimental and simulated, has been compared with the minimum in the effective interaction potential. In treating the effective colloidal interactions, we find that a straightforward, pairwise approach provides a reasonable description in describing the lattice parameter. The minimum in the effective interaction formed from combining the electrostatic repulsions and dipolar attractions is a useful means to approximate the lattice parameter, although close to melting fluctuations lead to a larger value in the lattice parameter than this minimum. Conversely, at high field strengths, our treatment appears to be less accurate. Apparently, higher order terms which we have not accounted for may become important, such as nonlinear Poisson–Boltzmann contributions to the electrostatic interactions, leading to deviations from the Yukawa form [Eq. (1)] (Ref. 22) or limitations in our pairwise treatment of the dipolar attractions.²³ Other possibilities include inaccuracies in our assumptions for the effective colloid charge [Eq. (3)], limitations of the 2D behavior of the experimental system. Perhaps due to a cancellation of errors, at high field strengths, the minimum in the effective interaction can sometimes provide a more accurate value of the lattice parameter than the simulations.

Another important assumption lies in our derivation of the electrostatic interactions. While their Yukawa-like form is well-accepted,²⁵ the values of the effective colloid charge comes from Eq. (3). We note that the Debye length we determine seems rather constant across the four particle sizes considered [Fig. 5(a)], which suggests that our approach is at least consistent. However challenging it may be, a more quantitative measurement of the local ion concentration in the vicinity of the crystalline rafts is desirable and will be considered in the future. Furthermore, there may be some variation in the value of Z_{eff} . In fact this should affect all state points in a similar manner (for each particle size), therefore, we anticipate a similar outcome, but that a different value might be arrived at in the fitting of the Debye length. However, owing to the relatively short-ranged nature of the interaction, the effect of a different value for the effective charge is unlikely to impinge significantly the Debye length and should have a negligible effect on our main results.

We also assumed that a given system is described by *one single* Debye length. In fact, in the counterion-dominated regime, the Debye length is a function of colloid concentration,³⁵ an effect we neglected. This might lead to a tightening at higher colloid concentration (i.e., high field strength), which may be expected to lead to an increase in deviation with the experimental results (Figs. 7 and 8). Nevertheless, varying the Debye length as a function of local colloid concentration would be worth considering in the future.

We extended our approach to a range of colloid sizes, to optimize the lattice tunability for display applications. Tunable 2D crystal rafts can behave as tunable diffraction gratings capable of filtering white light into visible colors.¹¹ Similar tunable diffraction has been proposed for display devices.³⁶ The range of colors obtainable for a given geometry is governed by the lattice tunability. Figure 9(b) demonstrates that lattice tunability in our system is maximized for particles of approximately 1–1.5 μm . Only higher field strengths applied to smaller particles can increase the lattice tunability. As already indicated, higher field strengths are not practical in the current experimental system, however, in future experiments metal coated colloids would exhibit much stronger dipolar interactions, enabling a reduction in field strength for a given attraction. Regardless, our methodology illustrates using the well-developed machinery of effective colloidal interactions as a means to model potentially complex interactions, useful for engineering purposes.

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