Anisotropic elasticity of experimental colloidal Wigner crystals

Emily R. Russell,1,* Frans Spaepen,2 and David A. Weitz1,2

1Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA
2School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

(Rceived 8 October 2014; published 17 March 2015)

Colloidal particles interacting via a long-range repulsion can, in contrast to hard-sphere systems, exhibit crystalline ordering at low volume fraction. Here we experimentally investigate the structure and properties of such “colloidal Wigner crystals.” We find a body-centered-cubic crystalline phase at volume fractions of \( \phi \gtrsim 15\% \), which exhibits large fluctuations of individual particles from their average positions. We determine the three independent crystalline elastic constants and find that these crystals are very compliant and highly anisotropic.

DOI: 10.1103/PhysRevE.91.032310

I. INTRODUCTION

Colloidal particles are often used to model atomic and molecular crystals, from the face-centered-cubic crystals formed by monodisperse hard-sphere or near-hard-sphere particles [1], to more complex crystal structures formed by heterogeneous mixtures of particles [2]. Colloidal crystals can also form at low volume fraction in a system with long-range repulsion [3–12]. These crystals exhibit a body-centered-cubic (BCC) structure and are often called colloidal “Wigner crystals,” in analogy to the minimum-energy configuration of electrons in a metal at low density and low temperature predicted by Eugene Wigner [13]. These crystals can be modeled by a screened-Coulomb or Yukawa potential [14,15] and have been found to be extremely soft [5–7]. Yet only anisotropic.

Particles of poly-methyl-methacrylate (PMMA; 1.8-μm diameter) coated with a brush of poly-hydroxystearic acid (PHSA) are suspended in a nonpolar solvent mixture of decahyronaphthalene (decalin) and tetrachloroethylene (TCE). The solvent ratio (roughly 55% decalin/45% TCE by volume) is chosen to match the mass density of the particles and hence to minimize the effects of gravitational pressure. The particles are fluorescently dyed, and the refractive index of the solvent mixture is sufficiently close to that of the particles to permit imaging in three dimensions using confocal microscopy.

A long-range repulsion between particles is introduced by the addition of 10 mM of the surfactant dioctyl sodium sulfosuccinate (commonly known as aerosol-OT or AOT). Above its critical micelle concentration (≈1 mM), AOT forms micelles, of radius on the order of 1.5 nm; these micelles act as charge carriers in the solution, with roughly one in \( 10^7 \) micelles acquiring a single elementary charge [16]. They furthermore enable the dissociation of the PHSA groups on the surface of the particles, with the dissociated proton entering a micelle core, so that the particles acquire a negative charge and the interparticle interaction becomes repulsive [16]. The 10-mM concentration was chosen to generate an optimum balance between highly charged particles (at large [AOT]) and long screening lengths (at low [AOT]), in order to achieve large interparticle spacings; at this AOT concentration, we anticipate a charge-carrier concentration on the order of 4 nM, and a Debye screening length of \( \kappa^{-1} \approx 0.8–1 \mu \text{m} \) [16–18].

Samples are prepared at fixed volume fractions and allowed to equilibrate over eight days before observations. We obtain three-dimensional image stacks using confocal microscopy and employ standard analysis techniques [19,20] to obtain precise locations over time of each particle in the imaging volume [21].

II. EXPERIMENTAL

III. RESULTS AND DISCUSSION

Body-centered-cubic “colloidal Wigner crystals” formed over a range of moderate particle number densities of \( n = 0.054–0.085 (\mu \text{m})^{-3} \) (corresponding to volume fractions of \( \phi \approx 15–26\% \)) [22]. Samples were polycrystalline, with typical grain sizes between hundreds of micrometers and...
several millimeters; the number density within a single sample was not uniform but varied by about $\Delta n \approx 0.002 (\mu m)^{-3}$ across different grains. The crystals always formed with a (110) plane parallel to the coverslip; examples of single planes are shown in Figs. 1(a) and 1(b). This (110) plane has a stretched hexagonal structure and is the closest-packed plane of the BCC crystal. The orientation indicates a boundary effect in the formation of the crystals, but we found that in most samples, the boundary effects did not extend to the fluctuations or material properties. The BCC crystal gave way to a colloidal fluid at lower number densities of $n \lesssim 0.045 (\mu m)^{-3}$ [Fig. 1(c)].

Individual particles fluctuate significant distances from their positions in the average lattice. This is visible in single snapshots of the crystal [e.g., Figs. 1(a) and 1(b)], where both the average lattice and the deviations of particles from the average lattice are apparent. The dynamics of these fluctuations are also apparent from data collected over time, with particles moving on the timescale of seconds.

One measure of the degree of motion in the system is the mean-squared displacement (MSD) of particles over a delay time $\Delta t$:

$$\text{MSD}(\Delta t) = \langle (x(t + \Delta t) - x(t))^2 \rangle - \langle (x(t + \Delta t) - x(t))^2 \rangle, \tag{1}$$

with the average taken over all particles and all starting times $t$. In particular, the MSD at long delay times indicates whether the system behaves as a fluid or as a solid, and for a solid, indicates the time- and length-scales of the fluctuations of particles about their average positions. For a crystalline sample, we expect the MSD to increase linearly with time at short times, as the particles diffuse within the potential wells due to interparticle interactions, and then to reach a plateau at long times, as particles are localized on the lattice, and in the absence of lattice defects, unable to diffuse freely. Several examples of the mean-squared displacements for crystalline samples are shown in Fig. 2(a); the experimental resolution of 2 s is similar to the localization timescale, so that the short-time increase is barely captured, but the plateau region is clearly apparent. The value at which the root-mean-squared displacement (RMSD) plateaus, $\sqrt{\delta r}$, can be considered as a “localization lengthscale” of the fluctuations. In some samples, the MSD increases again at later times, suggestive of particles slowly diffusing through the crystal; this could be the result of particles moving to different lattice sites, but our analysis is not conclusive.

The unitless Lindemann parameter $\delta_L$ gives the RMSD from the average position, $\langle \delta r \rangle$, as a proportion of the nearest-neighbor spacing $a$: $\delta_L \equiv \delta r / a \approx \delta r / (\sqrt{2}a)$. This parameter is associated with the assumption of Lindemann, commonly reformulated to state that the value of this proportion at melting is a constant for monatomic solids; this assumption has been observed to be a good correlation for many elemental metals with cubic structures, with a critical value of $\delta_L \approx 0.07–0.1$ and is often interpreted as a melting criterion or law [23,24]. In these experimental colloidal Wigner crystals, the Lindemann parameter appears to be nearly constant with number density over the range investigated [Fig. 2(b)], with perhaps a slight increase at the lowest number densities. At all number densities, it is significantly larger than 0.1.

An average lattice can be fit to all the particle positions. The lattice is constrained to have a BCC structure, enforcing a single lengthscale and orthonormality of the cubic crystal axes. The lattice is then described by seven parameters: one lengthscale, for which we use the side length $l$ of the cubic unit cell; three angles representing the rotation of the cubic lattice directions with respect to the imaging coordinates, expressed as a $3 \times 3$ orthonormal rotation matrix; and the three-component offset vector giving the translation of the lattice origin with respect to the origin of the imaging coordinates. These seven parameters are calculated independently at
each timestep from the 3D locations of typically 1000–2000 particles in a single imaging volume.

The fit of the particle positions to a BCC lattice is good. We examine the constraint that the three lengthscales of the crystalline lattice are equal by calculating the overall uniaxial strain of the system in each of the three cubic lattice directions. Taking the sample at $n = 0.054 \, (\mu m)^{-3}$ as an example, we find a slight extension in the (lattice) $X$ direction, and a slight compression in the (lattice) $Z$ direction, but that the magnitude of the uniaxial strain in any dimension is less than 1%. Similarly, we examine the constraint that the crystalline cubic axes are normal by considering the overall shear of the system in each of the three cubic planes. We find slight shear strains in each component, but again less than 1%. Thus, we are confident that our description of the system by an average BCC lattice is valid. We further find that the definition of the average lattice does not change significantly if we use subsets of a 3D image to fit the lattice.

Using this average lattice, each particle can be identified with a nearest lattice position, and its displacement from that lattice position determined; the root-mean-squared average displacement from the lattice position, $\delta r_l$, provides a time-independent measure of the fluctuations in the crystal. This RMSD from the lattice position is then used to calculate another Lindemann parameter, $\delta L = \delta r_l/a$, to be compared to the value calculated using the temporal RMSD [Fig. 2(b)]. Curiously, these two measures of the mean-squared displacement give slightly different results. However, both calculations give large values of the Lindemann parameter and little variation with number density.

Local deformation of the lattice is quantified by the local strains. We calculate these strains from the locations of a central particle and its crystallographic nearest- and next-nearest-neighbors (up to 15 particles in total), by finding the value calculated using the temporal RMSD [Fig. 2(b)]. Curiously, these two measures of the mean-squared displacement give slightly different results. However, both calculations give large values of the Lindemann parameter and little variation with number density.

Local deformation of the lattice is quantified by the local strains. We calculate these strains from the locations of a central particle and its crystallographic nearest- and next-nearest-neighbors (up to 15 particles in total), by finding the value calculated using the temporal RMSD [Fig. 2(b)]. Curiously, these two measures of the mean-squared displacement give slightly different results. However, both calculations give large values of the Lindemann parameter and little variation with number density.

Local deformation of the lattice is quantified by the local strains. We calculate these strains from the locations of a central particle and its crystallographic nearest- and next-nearest-neighbors (up to 15 particles in total), by finding the value calculated using the temporal RMSD [Fig. 2(b)]. Curiously, these two measures of the mean-squared displacement give slightly different results. However, both calculations give large values of the Lindemann parameter and little variation with number density.

Thermal distributions of different strain components are used to determine different elastic moduli. A cubic crystal is characterized by three independent elastic constants: $c_{11}$, $c_{12}$, and $c_{44}$. The shear modulus $c_{44}$ is directly obtained from the distribution of shear strains $\{e_{xy}, e_{xz}, e_{yz}\}$ expressed relative to the cubic axes. The other elastic constants, $c_{11}$ and $c_{12}$, are obtained indirectly from two other moduli: the bulk modulus $B$, which is calculated from the distribution of dilatations $\delta \equiv e_{xx} + e_{yy} + e_{zz}$; and the “rotated shear modulus,” $\mu'_{\text{shear}}$, that is, the shear modulus in a coordinate system rotated by $45^\circ$ around one of the cubic axes (e.g., the lattice $Z$ axis), calculated from the shear strains $e'_{xy'}$ in the rotated frame. Then

$$c_{11} = B + \frac{4}{3} \mu'_{\text{shear}}, \quad c_{12} = B - \frac{1}{3} \mu'_{\text{shear}}.$$  

Example averaged strain energy distributions for the sample at number density $n = 0.054 \, (\mu m)^{-3}$ are shown in Fig. 3(b), with the fits giving the elastic moduli $c_{44} = 13 \, mPa$, $B = 7.7 \, mPa$, and $\mu'_{\text{shear}} = 5.4 \, mPa$. Note that the two shear moduli are different, that is, the shear modulus depends on the
These results are in qualitative agreement with several previous experiments. These experiments were carried out with smaller particles at higher number density; to make order-of-magnitude comparisons, we assume that the elastic moduli vary roughly linearly with number density, that is, the energy of interaction is of the same magnitude across systems [5]. Using this scaling, we find order-of-magnitude agreement of our $c_{11}$ with Young’s modulus measured from the variation of lattice constant with gravitational pressure [5]; of $c_{44}$ with an isotropically averaged shear modulus measured mechanically [7]; and of all three elastic constants with those obtained by measuring dispersion curves using light-scattering [6].

The anisotropy in our crystals is much larger than that found in these latter experiments, presumably due to our larger value of the interparticle spacing relative to the screening length $\lambda^{-1}$, quantified by the parameter $\lambda \equiv \kappa n^{-1/3}$; in our experiments, $\lambda \approx 5-6$, whereas $\Delta/c_{44} \approx 0.14$ at $\lambda \approx 4$ in the previous experiments [6].

Our experimental results do not agree with early lattice dynamics simulations [15], which found much larger anisotropies ($\Delta/c_{44} > 1.7$ for $\lambda \geq 1$); these simulations found the relation $c_{12} \approx c_{11}$, giving the large anisotropy, in contrast to the relation $c_{12} \lesssim c_{44} < c_{11}$ in our experiments. The source of this discrepancy is unknown.

The experimental results are largely reproduced by simple numerical estimates. We assume a Yukawa interaction

$$U/\text{particle} = U_0 \frac{1}{2} \sum_i \frac{\exp(-\kappa r_i)}{r_i} ,$$  

(3)

with the sum taken over neighboring particles, and $r_i$ the interparticle distance; we consider particles on a perfect BCC lattice, taking into account the interactions with 64 nearest neighbors (the first 6 neighbor shells). The value of the screening length, $\kappa^{-1} = 0.45 \mu m$, is chosen to reproduce the experimental values of the anisotropy at the same number densities, while the overall energy scaling factor $U_0 = 10^{-23} \text{Jm} \approx 60 (\text{eV} \cdot \mu\text{m})$ is chosen to obtain elastic constants of the same order of magnitude. The resulting numerical estimates for the elastic moduli and anisotropy are shown in Fig. 5.

The values $\kappa^{-1} = 0.45 \mu m$ and $U_0 = 10^{-23} \text{Jm}$ are in line with our expectations. Our a priori estimate of the screening length $\kappa^{-1}$ was on the order of $\approx 0.8-1 \mu m$, based on the added AOT concentration and the results of earlier conductivity measurements in particle-free AOT solutions [16,17]. We expect the addition of particles to decrease the screening length, as the additional counterions that dissociate from the particle surfaces contribute to the screening; indeed, we expect $\kappa^{-1}$ to decrease further with increasing number density, which is not accounted for in the simple numerical model. If we estimate an effective particle charge from the interaction strength, we find $Z^* \approx \sqrt{U_0 e_0} \approx 100 e$. This is a very rough order-of-magnitude estimate but is consistent with the effective charges reported in a number of earlier studies [16-18].

These numerical estimates reproduce many aspects of our experimental results (Fig. 4). Most notably, the increase in anisotropy with decreasing number density is similar. The elastic constants themselves increase with increasing number density as expected; the slower increase in the experimental...
FIG. 5. (Color online) Variation with number density of (a) elastic constants and (b) anisotropy, calculated using a simple numerical model of particles on a perfect BCC lattice interacting via a Yukawa potential. $U_0 = 10^{-23} \text{Jm}$, $\kappa^{-1} = 0.45 \mu\text{m}$. $c_{11}$, $c_{44}$, and $B$ are calculated directly; $c_{12}$ and $\mu'_{\text{shear}}$ are inferred from $c_{11}$ and $B$. The range of number densities is chosen to match our experimental results.

results compared to the numerical estimates may be a result of the experimental value of $\kappa^{-1}$ changing with number density as discussed above. The nonlinearity of the stress-strain relationship is also reproduced: relative to its value at small strains ($\delta \approx 0$), the numerical second derivative of system energy with respect to dilatation, $\partial^2 U/\partial \delta^2 \approx B$, is 24% smaller when evaluated at $\delta = 0.1$ (expansion) and 31% larger when evaluated at $\delta = -0.1$ (compression). The shear stress-strain relationship, in contrast, is quite linear even up to large strains of $e = 0.2$, with the second derivative of energy $\partial^2 U/\partial e^2 \approx c_{44}$ varying by less than 7%. We note, however, that the values of $c_{11}$, $c_{12}$, and $B$ given by the numerical estimates are larger relative to $c_{44}$ than are those values calculated from the experimental results. This may be an indication of the presence of many-body effects, which contribute to these bulk elastic constants but not to the shear elastic constant [29]; we discuss this possibility further below. The discrepancy may also be related to the nonlinearity in the bulk elastic constants; while the numerical estimates give $c_{11}$ and $B$ in the small-strain limit, the values obtained experimentally are a less well-defined average of the elastic constants over a range of strain values encompassing both expansion and compression. Yet for the most part, a very simple model captures the qualitative behavior of the experimental system and, in particular, the variation of the anisotropy with number density.

The Cauchy relation predicts that $c_{12} = c_{44}$ for the centrosymmetric BCC lattice with two-body Yukawa interactions [30]. Our experimental results suggest that $c_{12} < c_{44}$ at most number densities, suggesting the possible importance of many-body interactions, though the results are not conclusive. These results are similar to those found in earlier experiments on face-centered-cubic (FCC) crystals of charged colloids, where the violation of the Cauchy relation provided clear evidence that many-body effects are important in charged colloids at high volume fraction [29]. Our possible violation is of a smaller magnitude than that in the FCC crystals, likely because our particle volume fraction is lower. Violation of the Cauchy relation is just one source of evidence for many-body interactions in charged colloid systems: three-body effective forces have been predicted by numerical solutions

FIG. 6. (Color online) Normalized spatial autocorrelations of the strain components in a colloidal Wigner crystal. Correlation fields of (a) the uniaxial strain $\varepsilon_{xx}$, plotted in the $XY$ plane; (b) the shear strain $\varepsilon_{xy}$, plotted in the $XY$ plane; (c) the uniaxial strain $\varepsilon_{xx}$, plotted in the nearest-neighbor plane, parallel to, but $1/2$ a lattice constant offset from the plane in panel (a); (d) the shear strain $\varepsilon_{xy}$, plotted in the same nearest-neighbor plane. In panels (a)–(d), $\Delta r$ is restricted to lattice vectors, and particles associated with their nearest lattice position before calculating the correlation. (e, f) One-dimensional cuts of the correlation fields along several directions for (e) the uniaxial strain $\varepsilon_{xx}$ correlation and (f) the shear strain $\varepsilon_{xy}$ correlation. Red circles, the cut along the (cubic) $X$ axis (e) and $Z$ axis (f); black squares, the average of the cuts along the other two cubic axes; blue triangles, the average of the cuts along the other two cubic axes; blue triangles, the average of the cuts along the nearest-neighbor directions. All plots are for number density $n = 0.054 (\mu\text{m})^{-3}$; results for other number densities are similar.
to the nonlinearized Poisson-Boltzmann equation [31]; and
many-body forces have been measured directly in recent
experiments on isolated systems of just a few colloidal particles
under experimental conditions similar to ours [32].

Particle fluctuations are not independent, but have a
collective nature. This collective behavior is quantified by the
correlations of the fluctuations; in particular, we calculate the
spatial autocorrelation for each strain component:

\[ C_{\varepsilon_{ij}}(\Delta \mathbf{r}) \equiv \frac{\langle \varepsilon_{ij}(\mathbf{r}) - \langle \varepsilon_{ij} \rangle \rangle \langle \varepsilon_{ij}(\mathbf{r} + \Delta \mathbf{r}) - \langle \varepsilon_{ij} \rangle \rangle}{\langle \varepsilon_{ij}(\mathbf{r}) - \langle \varepsilon_{ij} \rangle \rangle^2}, \tag{4} \]

with the average taken over all reference positions \( \mathbf{r} \) and all
times \( t \). We restrict the displacements \( \Delta \mathbf{r} \) to the lattice vectors
and associate each particle with its nearest lattice position to
calculate the correlation; this avoids calculating correlations at
non lattice-vector displacements with very low statistics.
Examples of these correlations are shown in Fig. 6. These
fields show only short-range correlations of strains in the
system, over about 3 lattice spacings. That we do not observe
evidence of longer-range vibrational modes is consistent with
earlier experiments. Propagating transverse modes have been
predicted at long wavelengths [6,7], while modes with small
damping coefficients appear as resonant modes of externally
driven standing shear waves and are used to measure the
shear moduli of colloidal crystals [7,33]. More recently, the
transition from overdamped to propagating transverse modes
in aqueous BCC colloidal crystals was observed for the first
time [34]; however, such propagating modes are not observable
when the sample dimensions are too small [6,34], as we expect
to be the case in our experiments.

Finally, we note that the correlation fields are constant
across different number densities. For many examples of strain
component and direction, there is little variation or trend with
number density. This type of correlation field is characteristic of
the Wigner crystals over the range of number densities studied.

IV. CONCLUSION

We have observed that a charged-sphere system of colloidal
particles with long-range repulsion forms body-centered-
cubic colloidal “Wigner crystals” at low volume fractions of
\( \phi \gtrsim 15\% \), in contrast to hard-sphere crystals that form
face-centered-cubic structures only at much higher volume
fractions. The soft interactions in a colloidal Wigner crystal
permit large fluctuations of the particles within the crystal,
with typical root-mean-squared displacements up to \( \approx 20\% \)
of the nearest-neighbor spacing (Lindemann parameter of
\( \delta_L \approx 0.20 \)). This parameter is roughly constant over the range
of number densities observed. We also measure the thermally
activated local strains in the system as a measure of the
fluctuations and find that in spite of the long-range ordering,
the damping fluid restricts correlations in the strains to about
two to three lattice spacings; the correlations are also almost
uniform with volume fraction.

We measure the crystalline elastic constants \( c_{11}, c_{12}, \) and
\( c_{44} \) and find them all to be on the order of 10 mPa, emphasizing
the pronounced softness of these crystals. The crystals remain
strongly anisotropic at all number densities, as indicated by the
nonzero values of \( \Delta \equiv 2c_{44} - (c_{11} - c_{12}) \), with the anisotropy
increasing with decreasing volume fraction. These results are
qualitatively consistent with numerical estimates and with
values reported in the literature.

These colloidal Wigner crystals offer the opportunity to
study remarkably soft crystals with a structure uncommon
in colloidal systems, and to study both the unusually large
fluctuations and the material properties of this phase.

ACKNOWLEDGMENTS

Thanks to Jeroen Appel for synthesizing the PMMA
particles and to Nicholas Schade and Joe McDermott for
assistance with system characterization. Joris Sprakel carried
out the experiments which initially inspired this further work
[18], and we have benefited from conversations with him, with
Peter Schall, and with Jan Tobochnik. We also thank Katharine
Jensen for the use of her particle tracking and strain calculation
codes. This material is based upon work supported by the
NSF through the Graduate Research Fellowship (Grants No.
DGE-0946799 and No. DGE-1144152 to E.R.R.), Grants No.
DMR-1310266, No. DMR-1206765, and the Harvard MRSEC
(Grant No. DMR-0820484).

[1] P. N. Pusey and W. van Megen, Phase behaviour of concentrated
suspensions of nearly hard colloidal spheres, Nature 320, 340
(1986).
A. I. Campbell, A. Imhof, M. Dijkstra, R. van Roij, and A.
van Blaaderen, Ionic colloidal crystals of oppositely charged
suspensions of polystyrene spheres, Phys. Lett. A 48, 225
(1974).
[4] R. Williams, R. Crandall, and P. Wojtowicz, Melting of crys-
talline suspensions of polystyrene spheres, Phys. Rev. Lett. 37,
348 (1976).
[5] R. S. Crandall and R. Williams, Gravitational compression of
crystallized suspensions of polystyrene spheres, Science 198,
293 (1977).
Lattice dynamics of colloidal crystals, Phys. Rev. A 26, 2869
(1982).
[7] H. M. Lindsay and P. M. Chaikin, Elastic properties of colloidal
[8] L. K. Cotter and N. A. Clark, Density fluctuation dynamics in
a screened Coulomb colloid: Comparison of the liquid and bcc
Axe, and Y. Fujii, Complete phase diagram of a charged colloidal
colloidal model system to study long-range interactions
quantitatively in real space, J. Phys.: Condens. Matter 15, S3581
(2003).


[22] The number density is determined geometrically from the lengthscale of the best-fit lattice described later. The volume fraction is obtained from the number density assuming a particle diameter of 1.79 μm, measured using dynamic light-scattering on a dilute sample. The uncertainty in this diameter measurement, and in particular the uncertainty in the relation of the measured hydrodynamic diameter to the hard-sphere core diameter, may introduce a systematic error in the reported volume fractions.


