// Metal-like elasticity in colloidal crystals //

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In a recent study *(1)*, the elastic properties of single crystals consisting of charged colloidal particles were determined from real-space imaging experiments using confocal microscopy. The normal modes and the force constants of the crystal were obtained from the fluctuations of the particle positions around the lattice sites using the equipartition theorem. We show that the elasticity of the studied crystals is largely analogous to that of metals. Like the conduction electrons in metals, the small ions in the solvent of the colloidal crystals give rise to non-central forces between the big colloidal particles and, therefore, the Cauchy relation is not fulfilled.

Understanding how an elastic material deforms under external mechanical stresses is essential knowledge in material science and of fundamental interest. The elastic properties of a crystal as well as the interactions between the particles forming a crystal lattice are character-ized by force constants *(2,3)*. These relate the displacement of one particle from its equilibrium position to the force acting on a neighboring particle. In metallic and other hard crystalline materials a great deal is known about these microscopic forces and about elasticity. However, in soft materials such as colloidal suspensions the study of elasticity currently receives a lot of attention because of their great potential for the development of novel materials with tailored properties. Yet, the elastic constants of colloidal crystals have never been measured and the nature of the internal forces in colloidal crystals is largely unknown.

In analogy to metals, crystals of charged colloids *(4)* consist of mesoscopic, Brownian macroions in suspension that form a lattice and are surrounded by the much smaller microions. Like the electrons in metals, the microions are much more mobile than the large ions that form the lattice and, as a consequence, they always arrange in clouds around the macroions to screen their charges. Thus, in metals and crystals of charged colloids there are two species that move and respond on vastly different length and time scales. Therefore, the question arises whether these similarities manifest themselves in similar elastic properties despite the huge difference in the respective moduli.

Information on the nature of the interactions in colloids can be obtained by measuring the components of the tensor of elasticity. These are defined as the second derivatives of the elastic free energy of a crystal with respect to components of the strain tensor: $C_{\mu\nu\rho\sigma} = \partial^2F/\partial\eta_{\mu\nu}\partial\eta_{\rho\sigma}$ *(3)*. The number of independent components of $C_{\mu\nu\rho\sigma}$ depends on the point symmetry of the crystal; a crystal with the cubic *fcc* symmetry has only three independent elastic constants: C_{11}, C_{12}, and C_{44}, where the indices are given in Voigt notation *(3)*. In 1828 A.J. Cauchy found that the assumption of central forces between small volume elements of a crystal yields additional relations between the elastic constants and, therefore, further reduces the number of independent components in $C_{\mu\nu\rho\sigma}$ *(2,5)*; e.g. for a crystal with *fcc* symmetry $C_{12} = C_{44}$ for central forces. These relations are now known as Cauchy relations, and they allow the interesting conclusion that their violation must be due to non-central forces. Metals are a good example: Because of non-central forces due to the conduction electrons that screen the charges of the ions the Cauchy relations are not fulfilled *(2)*.

In a recent study *(1)* we have shown that the elastic constants of colloidal crystals and essential information about the interactions between the colloidal particles can be obtained best by real-space imaging experiments. The experimental means for this have recently become available with fast laser scanning confocal microscopes. As illustrated in Fig. 1, our 3D realspace imaging data allows the direct observation and quantitative analysis of the structure and dynamics of up to

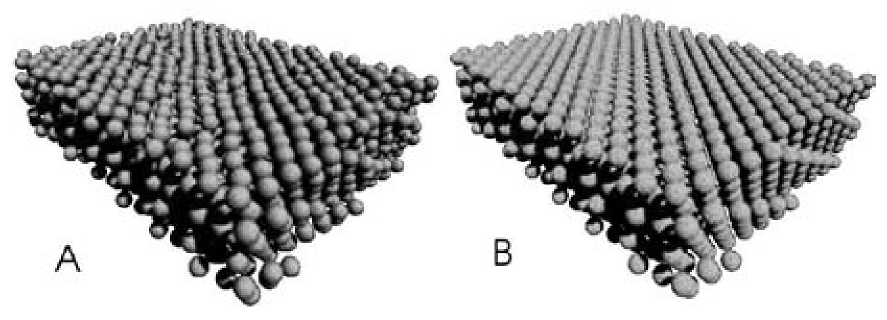

Fig. 1: (A) A snapshot of 1909 particles in a colloidal crystal with fcc symmetry. The image is obtained using the coordinates extracted from 100 2D microscopy images.
(B) A time average of the same crystal as shown in (A) calculated from 98 snapshots. The high quality of the crystal is apparent. In comparison with (A) the fluctuations of the particles around their equilibrium positions can be visualized.

10^4 micron-sized particles. From measurements of colloidal mono-crystals with *fcc* symmetry we extract the force constants of the crystal from the dispersion curves of overdamped normal modes and, in the $q \to 0$ limit, all elastic constants of the crystal. Our results show that the interaction between the colloidal particles in the crystal cannot be described in terms of central forces, but non-central forces acting between the macroions make the elastic response of the studied colloidal crystals similar to that of metals. In metals, the force constants can be determined with scattering methods such as inelastic neutron scattering that probe the normal modes of the lattice. However, in colloidal crystals scattering methods such as dynamic light scattering (DLS) do not yield the same information *(6,7)*, because the solvent of the suspension strongly damps the motion of the colloidal particles and, therefore, prevents the existence of propagating lattice normal modes. As a consequence, in scattering experiments, the force constants are always intertwined with the complicated, wave-vector dependent frictional forces with the solvent. In contrast to DLS, hydrodynamics does not play any role in the determination of the lattice normal modes from the real-space imaging data. Our method *(8)* relies exclusively on "snapshots" of the particle positions that are used to calculate ensemble averages and, therefore, the frictional forces between the colloidal particles and the solvent never enter our analysis.

We used poly-methylmethacrylate spheres *(9)* with a diameter $\sigma = 1.66\ \mu m$ that were fluorescently labeled with rhodamine and suspended in a solvent matching both density and refractive index of the particles. The particles were observed with a fast laser-scanning confocal microscope using a 100 × objective lens to observe a volume $V \approx 58\ \mu m \times 55\ \mu m \times 20\ \mu m$ inside the much larger sample cell. The objective was mounted on a piezo translation stage for the scanning in z-direction and, typically, 5000 particles were observed in one 3D snapshot. It took ≈ 1.5 s to observe the whole volume V. After the experiment, the particles are detected by looking for local intensity maxima and their positions can be determined with an accuracy of ≈ 20nm *(10)*. Samples with volume fractions $0.01 < \phi < 0.41$ were prepared in order to map out the phase behavior at room temperature; all measurements were carried out at $T = 295K$. Crystallization was observed in samples with volume fractions larger than $\phi_f \approx 0.31$. The phase behavior compares well with that of hard spheres with Yukawa repulsion (HSY) with the interaction potential $V(r) = V_{HS}(r) + \frac{B\sigma}{r} \exp(-\kappa [r - \sigma])$ *(11)*. Here, $V_{HS}(r)$ is the hard sphere potential, $\kappa^{-1} = 221 \pm 30nm$ is the Debye screening length, and $B = k_B T \frac{\lambda_B}{\sigma} \left(\frac{Z_{eff}}{1+\kappa\sigma/2}\right)^2 \approx 12 k_B T$ is the contact value with the Bjerrum length λ_B and the charge number $Z_{eff} = 245 \pm 40$.

For $\phi \geq 0.31$ large random hexagonal close packed crystals *(12)* with hexagonal planes oriented parallel to the cover slip formed within several days, and we chose regions of three to ten hexagonal layers with *fcc*-stacking for our measurements. The lattice constant *a* of the Bravais unit cell was measured, and the structure of these crystals was compared with a perfect *fcc* lattice. As illustrated by Fig. 1B, the deviations of the average particle positions from the *fcc*-lattice positions are small. For the calculation of the displacement $\mathbf{u}_i(t) = \mathbf{r}_i(t) - \mathbf{R}_i$ of particle *i*, the reference position $\mathbf{R}_i$ is determined by averaging its position over all snapshots taken during the measurement. The distributions of the components u_μ of the displacements are found to be Gaussian at all volume fractions, so we are always in the harmonic regime of crystal elasticity. Following essentially the same procedure as in Ref. *(8)*, the dynamical matrix $D_{\mu\nu}(\mathbf{q})$ *(2)* is determined using the equipartition theorem; each **q**-mode of the harmonic approximation $U = \frac{1}{2}\Sigma_{\mathbf{q},\mu,\nu}\, u_\mu(\mathbf{q})\, D_{\mu\nu}(\mathbf{q}) u^*_\nu(\mathbf{q})$ to the elastic energy of the crystal contains the thermal energy $k_BT/2$. Therefore, the inverse of the dynamical matrix can be obtained from an ensemble average of the measured particle displacements:

$$D^{-1}_{\mu\nu}(\mathbf{q}) = \frac{\langle u_\mu(\mathbf{q}) u^*_\nu(\mathbf{q})\rangle}{k_BT} \qquad (1)$$

We calculate the ensemble average ⟨...⟩ by taking a time average over all measured configurations and we analyze modes with wave vectors $\mathbf{q} \propto (1, 1, 0)$, (1, 1, 1), and (1, 0, 0). Since these directions in reciprocal space correspond to symmetry axes of 2-, 3-, and 4-fold rotations, the eigenmodes in these directions are a longitudinal mode *l* and two transverse modes t_1 and t_2 with eigenvectors $\hat{e}_l$, $\hat{e}_{t1}$, and $\hat{e}_{t2}$, respectively. As shown in Fig. 2, we obtain the modes *l*, t_1, and *s* with propagation $\mathbf{q} \propto (1, 1, 0)$, t_1 and m for $\mathbf{q} \propto (1, 0, 0)$, and t_1 and *m* for $\mathbf{q} \propto (1, 1, 1)$. Here, *s* denotes a combination of the modes t_1 and t_2, and *m* refers to a combination of longitudinal and transverse modes. The full lines represent fits with general force constants of an *fcc* lattice with interactions up to 3rd nearest neighbors. Three force constants ($A^{(1)}_{11}$, $A^{(1)}_{12}$, $A^{(1)}_{33}$) determine the forces between nearest neighbors, while two ($A^{(2)}_{11}$, $A^{(2)}_{22}$) and four ($A^{(3)}_{11}$, $A^{(3)}_{12}$, $A^{(3)}_{13}$, $A^{(3)}_{22}$) constants define the forces acting on the 2nd and 3rd neighbors, respectively (2). The absolute values of the 3rd order constants $A^{(3)}_{\mu\nu}$ are found to be ~ 0.01 $|A^{(1)}_{11}|$; they are not essential for the quality of the fits. For a radially symmetric interaction, the force constants fulfill the condition $\Gamma := A^{(1)}_{12} / (A^{(1)}_{11} - A^{(1)}_{33}) = 1$ *(2)*. However, from the measurements we find $\Gamma < 0.25$ at all ϕ. This is clearly incompatible with a pairwise additive, radially symmetric interaction. Furthermore the determined force constants differ strongly from those expected for a HSY-crystal. E.g.

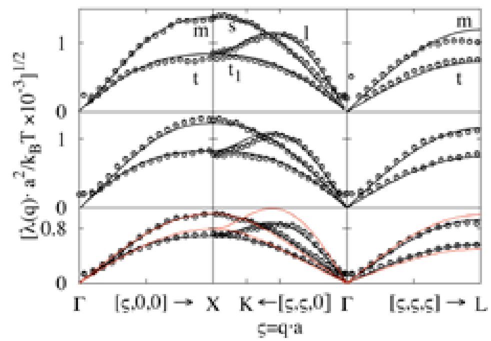

Fig. 2: Measured dispersion relations for (top to bottom) ϕ = 0.38, 0.34, and 0.31. The full lines represent fits to the data. K, X and L denote the edge of the 1st Brillouin zone in (1, 1, 0), (1, 0, 0), and (1, 1, 1)-direction, respectively. For each column, the modes are identified in the topmost panel. For comparison, the dispersion relations for a HSY crystal with B = 15 k_BT and $\kappa\sigma$ = 8 are shown by the dotted lines for ϕ = 0.31. See text for details.

a displacement of the particle at (0, 0, 0) in the (1, 0, 0)-direction strongly attracts the 2nd neighbor at (*a*, 0, 0); this behavior is a consequence of many body forces and cannot be accounted for by the HSY interaction or any other radially symmetric pair potential. Potential error sources such as random errors in the particle coordinates, the effect of the finite scanning speed, the limited number of snapshots in a measurement, and the size of the observed volume V were assessed by comparing the measurements with MC simulations. The measurements were found to give reliable results *(1)*.

Therefore, we can determine all elastic constants of a colloidal crystal from a single measurement. In the $q \to 0$ limit, we obtain the tensor $B_{\mu\nu\rho\sigma}$, which connects stress and strain: $T_{\mu\nu} = B_{\mu\nu\rho\sigma}\,\varepsilon_{\rho\sigma}$. For crystals under stress, $B_{\mu\nu\rho\sigma}$ is not the same as the tensor of elastic constants $C_{\mu\nu\rho\sigma}$, which is defined via the elastic free energy *(3)*. The studied crystals are under stress due to the pressure p in the sample cell; for *fcc* symmetry the two tensors are connected by the relations $B_{11} = C_{11} - p$, $B_{12} = C_{12} + p$, and $B_{44} = C_{44} - p$ with the indices given in Voigt notation *(3)*. For central forces and cubic lattices, the condition $\Gamma = 1$ is a consequence of the Cauchy relation $B_{12} = B_{44} + 2p$. Elastic constants $B_{\mu\nu}$ and elastic moduli representative of all our results are shown in Table 1 along with values for a HSY crystal. Since $B_{44} > B_{12}$ and $p > 0$, our measurements clearly contradict the Cauchy relation, while it holds in HSY crystals. In analogy to metals, the non-centrality of the forces affects mostly the bulk modulus $K = (B_{11} + 2B_{12})/3$, while the shear moduli $G_1 = B_{11} - B_{12}$ and $G_2 = B_{44}$ have similar values in the studied crystals and HSY crystals. The value of K obtained from experiment is almost a factor of 3 smaller than for the HSY crystal. These observations corroborate that the micro-ions in crystals of charged colloids play a role similar to the electron gas in metals.

Our main results are the incompatibility of the force constants with any effective, radially symmetric pair-potential and the importance of many-body forces. The elastic properties and the behavior of the lattice normal modes in the studied colloidal crystals are rather metal- than HSY-like. Moreover, we note that direct observation of colloidal crystals yields the results that are obtained by e. g. inelastic neutron scattering in hard materials. Our methods are not limited to charged colloids but allow to study the elastic properties of various colloidal crystals that can be treated in the harmonic approximation.

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$\left(\frac{k_B T}{\sigma^3}\right)$	B_{11}	B_{12}	$B_{44} = G_2$	G_1	K
$\phi = 0.38$	67	17	65	50	33
$\phi = 0.34$	56	13	36	43	27
$\phi = 0.31$	28	9	28	19	15
HSY, $\phi = 0.31$	63	48	25	15	53

Table 1: Elastic constants $B_{\mu\nu}$ with indices given in Voigt notation and elastic moduli obtained from experiment and from a calculation for a HSY crystal ($B = 15\,k_B T$, $\kappa\sigma = 8$).

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