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Modes of Motion of a Colloidal Crystal

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The dynamical behavior of charge-stabilized colloidal crystals that consist of polystyrene spheres in highly deionized water is determined by solvent flow mediated interactions and by ionic effects. The expression of these effects strongly depends on the polarization of crystal waves. Using dynamic light scattering we trace all but the fastest known modes of motion and evaluate the influence of ion friction. We find a new mode that we ascribe to ion retardation. Our experiments point to the importance of electrophoresis for microscopic colloid dynamics.

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A colloidal crystal is a dispersion of macroscopic particles that has crystalline order. As the typical size of an elementary cell is \( O(\mu m) \), a polycrystalline sample shimmers iridescently in visible light. Charge-stabilized colloidal crystals are model systems for studying structural phase transitions such as freezing and melting. These processes can even be studied in real space, for example by near-field microscopy [1]. Colloidal crystals are also well-characterized model systems for precise studies of fundamental interactions in colloids. In this case, light scattering is superior as it provides direct access to reciprocal space.

Our colloidal crystals consist of a dilute suspension of charged polystyrene spheres in highly deionized water. They are surrounded by clouds of counterions which screen the bare Coulomb field. The spheres are agitated by Brownian forces and they interact both directly through electrostatic forces and indirectly through the flow of the intervening solvent fluid. Electrical interaction also arises because of the dynamical behavior of counterions.

Careful dynamic light scattering experiments on such crystals were done by Hurd et al. who showed how to extract crystal dynamics from measured correlation functions [2]. Although hydrodynamic interaction in dilute colloidal crystals is well understood [3,4], the effect of electrodynamic forces is the subject of controversy. The vanishing relaxation rate of transverse phonons at the Brillouin zone center that was found in [2], was ascribed to ion retardation effects by Felderhof and Jones [5]. However, in [6] it was found that the finite thickness of Hurd’s crystals had a similar effect on the relaxation rate. It is our aim to unravel this delicate interplay of fluid and ion flow through measuring the relaxation of the associated crystal modes.

Colloidal crystals with lattice parameter \( R_0 = 0.75 \mu m \) (volume fraction \( 2.48 \times 10^{-3} \)) were grown in a solution of \( a = 52 \text{ nm} \) radius polystyrene spheres in highly deionized water. We assume the deionization to be effective, so that no residual \( K^+ \) salt ions are present. At these low concentrations, the spheres order in a bcc lattice and single crystals with a typical size of a few mm can be obtained. While the lattice constant can be found accurately from the angular position of Bragg reflections, determining the charge on the sphere is more difficult. Our crystals border on the melting transition and the upper part of our cell contains liquid-phase colloid. We have determined the sphere charge \( Z \) in the liquid phase through measurement of the static structure factor [7] and using a representation by Hayter et al. [8] with \( Z \) as a free parameter. The found number of elementary charges was \( Z = 360 \pm 20 \), which places our crystals within the quoted error on the melting curve predicted by Robbins et al. [9]. The availability of a good estimate for the charge will prove to be essential.

Figure 1 is a schematic overview of our experiment. In order to prevent multiple scattering, the crystals are contained in a thin-film cell. Its 103.1 \( \mu m \) thickness is

![Figure 1. View (not to scale) of the experimental setup. The colloidal crystal is contained in the thin-film cell. A laser beam is focused in the cell. Light scattered off the crystal is mixed with a fraction of the incident light which is transported through a monomode optical fiber; this ensures unambiguous heterodyne scattering. Beam splitters are indicated by \( D \), a beam combiner by \( C \). Scattered light with scattering wave vector \( k_s \) is selected through pinhole \( P \) and sent into a (multimode) optical fiber that acts as a second pinhole. It is transported to two photomultipliers whose photopulses are fed to a digital correlator which is operated in the cross-correlation mode. Usage of optical fibers greatly facilitates access to reciprocal space.](image)
gauged interferometrically, and is uniform up to 0.1 μm. The crystal is illuminated by a 30 mW HeNe laser beam at λ = 632.8 nm that is operated from a stabilized power supply. Light scattered by the crystal is mixed with a small fraction of the incident beam. This local oscillator is strong enough to overwhelm light that is unambiguously scattered off cell surfaces, and eliminates the inherent ambiguity of a homodyne setup where only the scattered light intensity is registered.

The reference beam is transported through a polarization preserving monomode optical fiber, which allows large freedom in the selection of scattering angles. The scattered light is angle selected through pinholes, transported through a (multimode) optical fiber, and sent through a beam splitter to two photomultiplier tubes whose photopulse outputs are analyzed with a digital correlator operated in the cross-correlation mode. This operation mode is needed for accurate timing statistics of fast fluctuations.

The bcc crystals grow with their closest-packed plane parallel to the cell wall. By a judicious choice of the cell orientation and scattering angle, it is possible to select both wave vector and polarization of detected lattice waves. Thus we have studied longitudinal waves in the [110] direction and (long-wavelength) transverse waves in the [100] direction; we believe that considering other geometric arrangements will not give significant additional information. As we are interested in long-wavelength phonons, pure crystals with sharply defined Bragg spots were needed. An automated procedure has been developed to accurately track single crystals and compensate for refraction at interfaces when the cell is rotated.

For a better appreciation of our experimental findings, let us briefly summarize the elementary crystal interactions. To this end we write the deviation $s_i$ of sphere $j$ from its equilibrium position $R_j$ as a sum over vibration modes $a_q$, $s_j = \sum_q a_q \exp (i q \cdot R_j)$. We further assume harmonic time dependence $a_q (\omega)$. The equation of motion for a single mode $a_q$ then is $M(q, \omega) \cdot a_q (\omega) = X_q (\omega)$ with $X_q$ the (spectrally white) Brownian force. The dynamical matrix $M(q, \omega)$ is

$$M(q, \omega) = \left[ -\omega^2 I - \frac{D(q)}{m} - \frac{i \omega}{m} T(q)^{-1} \right],$$

with $I$ the unit matrix and $m$ the mass of sphere. The hydrodynamic friction force is contained in the lattice transformed Oseen tensor $T$. It consists of the single sphere Stokes friction force $-i \alpha \omega \eta \pi a^2 \eta$, with $\eta$ the solvent viscosity, but many-body hydrodynamic interaction also significantly contributes, even in dilute crystals. All electric interactions are grouped into the matrix $D$ that embodies both direct electrostatic interactions between charged spheres and electrodynamic interactions due to the motion of the countermions that surround the spheres.

For the [100] and [110] directions of interest, the matrix $M$ can be diagonalized trivially. Measured scattered-light correlation functions for longitudinal and transverse polarizations are the sum of exponentials $G^{L,T}(q, t) = \sum \alpha_j \exp (i \Gamma_j t)$ where $\Gamma_j$ are the roots of the corresponding characteristic equations $\|M^{L,T}(q, \Gamma_j)\| = 0$. The prefactors $\alpha_j$ are proportional to $\Gamma_j^{-1}$ and alternate in sign (with $\alpha_1 > 0$). The modes of motion of a colloidal crystal are almost always overdamped with purely imaginary $\Gamma_j$.

A key aspect of this Letter is the influence of electrodynamic forces. When a sphere moves, the counterion cloud that surrounds it lags behind and relaxes through ion diffusion. Similarly, when other spheres move, the resulting dipole field exerts a force on the ions. This leads to extra friction. It was pointed out in [5] that the induced dipole forces remain in the zero wavelength limit, which would have a marked influence on the damping of shear waves at $q = 0$. The ion retardation effect, however, can be counteracted by convection of the ions with the moving solvent fluid, an effect that was not considered in [5].

It is illustrative to first discuss the modes of motion for the case of pure hydrodynamic interactions where the spheres have a static screened Coulomb potential interaction $-\varepsilon^2 Z^2 \exp (-kr)/4\pi \varepsilon_0 r$, with $\varepsilon$ the dielectric constant and $\kappa^{-1} = 0.25 \mu m$ the Debye length. Because the transverse friction matrix contains the factor $\omega - i q^2 / \rho$, the characteristic equation for transverse modes $\|M^T(q, \omega)\| = 0$ is third order for purely hydrodynamic interactions. Thus, there are three different modes of motion, but they have vastly different relaxation constants. The first mode $\Gamma^T_1$ is $1/\tau_{VAC} = 6 \pi \eta a / m$ is the fast decay $[O(10^9)$ Hz of the autocorrelation function of the Brownian velocity; it is unobservable in our experiment. The second mode $\Gamma^T_2(q) = \eta q^2 / \rho$ is the relaxation of hydrodynamic shear waves. The existence of this mode was verified in our experiment and the measured dispersion agreed well with the predicted $\eta q^2 / \rho$. This is a purely hydrodynamic mode; the crystal acts as a mere tracer of solvent shear fluctuations.

In Fig. 2 we show the dispersion curve of the third and slowest transverse mode $\Gamma^T_3(Q)$. At small reduced wave number $Q$, there is no relative motion of spheres and fluid, and the friction $\eta q^2 / \rho$ that crystal waves experience is merely that of hydrodynamic shear waves. The apparent small-$Q$ asymptote corresponds to the approximate zero $\Gamma^T_3 = \rho D^T(q)/m_F \eta q^2$, where $m_F$ is the mass of fluid in a unit cell. The absence of the sphere size in this expression again illustrates that in the long-wavelength limit spheres and fluid move in concert. The asymptote is reached because $D^T(q) \sim q^2$ for $q \rightarrow 0$. Very close to the zone center, this mode gives way to one that is propagating.

The calculated dispersion function agrees well with the experimental data [10]. The predicted transition to propagating modes at $Q = 0.0027$ lies outside our experimental wave number resolution. It was argued in [6] that at such small wave numbers the quantization of hydrodynamic modes in the approximately 100 μm...
wide cell gap introduces extra damping. Observation of propagating modes requires a (much) wider gap. Reaching small wave numbers, however, is difficult as scattered light must be detected very close to Bragg reflections and large perfect crystals are needed.

The behavior of the dispersion curve is dramatically altered when including the effect of ion friction. As was pointed out in [5], the relaxation rate now vanishes at the zone center. Our experimental data are in qualitative disagreement with this prediction and instead follow more closely the prediction based on hydrodynamic friction only. The reason for this discrepancy is most probably the neglect of ion convection in the theory. Because there is no relative motion of spheres and fluid near $Q = 0$, ion retardation effects should be much smaller than predicted with a model that ignores convection [11].

For the longitudinal modes, the incompressibility condition of the solvent flow field precludes the factor $(\omega - i\eta q^2/\rho)$ and the characteristic equation for pure hydrodynamic friction has, apart from the fast $\Gamma_1^L = \tau_{\text{AC}}^{-1}$, a single remaining zero at $\omega = i\Gamma_2^L$. Figure 3 shows the measured dispersion function $\Gamma_1^L(Q)$ of longitudinally polarized phonons in the [110] direction. Because for this mode of motion, relative motion of spheres and fluid persists at the zone center, the damping at $Q = 0$ is the simple Stokes friction and the relaxation rate should vanish as $\sim Q^2$. The overall form of the prediction is in good agreement with the experiment, but details differ. Figure 3 also demonstrates that, even for such dilute crystals, multibody hydrodynamic effects are strong. However, in order to extract precise information on multibody hydrodynamic interaction in experiments on colloidal crystals, precise information on the sphere charge is needed. The shown theoretical results include ion retardation, but its effect on the longitudinal damping is negligible.

Near the Brillouin zone center, our measured relaxation rates tend to an apparent offset at $Q = 0$ of approximately 200 Hz. These phonons could be followed to $Q \approx 0.02$; at smaller wave numbers the measurement of such slow relaxation rates becomes increasingly difficult due to low-frequency noise [12]. Still, our data significantly deviate from the predicted $\Gamma_1^L(Q) \sim Q^2$ for $Q \approx 0.05$. We do not have an explanation for these findings; perhaps they can be explained by the slow annealing of lattice defects.

Close scrutiny of the longitudinal correlation functions teaches that, apart from the pure hydrodynamic modes $\Gamma_1^L$ and $\Gamma_2^L$ there is an intermediate mode which is not predicted by the theory. Figure 4 shows the correlation function $G^L(t)$ very close to the zone center ($Q = 0.015$) and at short time delays. Superposed on the sloping background that corresponds to the slow $\Gamma_3^L$ mode, an inverted exponential can be seen that is caused by a new fast mode. The dispersion $\Gamma_2^L(Q)$ of this mode is shown in Fig. 5. It shows a conspicuous linear behavior and it appears to have a zero at a finite value of $Q$.

This mode has not been found earlier in colloidal crystals and we ascribe it to ion dynamics. The theory [5] for ion retardation effects also predicts a longitudinal and transverse ion mode, but it has a $Q$-independent relaxation rate which is the reciprocal of the time the ions need to diffuse over a Debye length $\kappa^{-1}$, $\Gamma = D_i \kappa^2 = 1.3 \times 10^5$ Hz, with $D_i = 7.5 \times 10^{-9}$ m$^2$ s$^{-1}$ the counterion diffusion coefficient. Although the relaxation rate has the right order of magnitude, its predicted $Q$ independence and its occurrence in transverse modes disagrees with the experiment.
Because for longitudinal phonons relative motion of solvent and spheres remains at $Q = 0$, it is not surprising that the small-$Q$ behavior of an ion retardation mode has longitudinal polarization. Ion convection makes it improbable that such modes exist in the long-wavelength transverse case.

In conclusion, ion retardation effects play a subtle role in the dynamics of lattice waves of colloidal crystals. We have searched for it in the known modes of motion, and have found a new mode that we ascribe to the effect of ion motion. Its polarization can be explained by considering the effect of electrophoresis, i.e., the coupling between the internal crystal electric field and solvent flow. There is a clear need for a theory that can explain the observed wavelength dependence of this new mode [13].

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[10] The lattice transform $D^T(Q)$ of the elastic shear matrix was done by summing screened Coulomb intersphere potentials $\phi = -Z^2e^2 \exp(-kr)/r$ over shells of neighboring spheres up to a distance $R_0/\sqrt{2}/2$ of the reference sphere. Merely considering nearest (as was done in [2]) or next-nearest neighbor interactions (as was done in [5]) led to large errors in the elasticity.
[11] We have found that it is possible to extend the theory of [5] in a consistent way with a convection contribution and derive (analytic) solutions that predict a significant reduction of ionic friction. In our calculation we assumed that the motion of a given sphere induces convection of the background ion distribution through the Oseen flow field of that sphere. Such a description is only approximate because convection is, instead, induced by the full many-body flow field.
[12] As was already noticed in [6], and as is evident from Fig. 4, measured correlation functions are markedly non-exponential on time scales $1/\Gamma_1$. We have found $\Gamma_1$ by representing $G^l(t)$ by $G^l(t) = c_1 - c_2t + c_3(t + c_4t^2 + c_5t^3) \exp(-\Gamma_1t)$, and determining the constants $c_i$ in a least squares procedure.
[13] E. A. Allahyarov, L. I. Podloubny, P. P. J. M. Schram, and S. A. Trigger, Phys. Rev. E 55, 592 (1997), explain the fast longitudinal relaxation as the manifestation of a finite crystal thickness effect. However, for this explanation to work, a much thinner crystal ($11 \mu m$) had to be assumed than was used in the experiments ($103.1 \mu m$).