Low energy modes and Debye behavior in a colloidal crystal

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Abstract. - We study the low energy modes of a three dimensional colloid recorded using confocal microscopy to study the lattice vibrations. This is done in a two-dimensional cut through a three-dimensional crystal. We find that the observed density of states is incompatible with the standard Debije form in either two or three dimensions. These results are confirmed by numerical simulations. We show that an effective theory for the projections of the modes onto the two-dimensional cut describes the experimental and simulation data in a satisfactory way.

Introduction. Colloidal particles dispersed in a solvent form fluid and solid phases under appropriate conditions [1,2]. The ordered phase is interesting due to their long-range order combined with very soft mechanical properties making thermal fluctuations very important. For the colloidal systems considered here, the shear modulus is only a few Pa, whereas crystalline solids typically have moduli in the GPa range [3,4]. Comparison of the properties of colloidal systems with harder molecular solids is a matter of ongoing research [5–7]. Earlier studies have largely focused on the the phonon dispersion behavior measured by means of video microscopy [5] or light scattering [8,9]. However, to our knowledge there is no experiment that directly verifies the Debije scaling in the measured density of states of the vibrational modes. Even for molecular crystals, the Debije behavior has proven rather hard to measure directly; mostly neutron scattering experiments have provided some data that agree with the expected ω^2 behavior [10]. Perhaps for this reason the temperature dependence of the specific heat is taken as the hallmark of Debije behavior for normal crystalline solids at low temperatures. The question we ask in this Letter is how the spectrum measured in a colloidal crystal compares with the predicted Debije behavior, $D(\omega) \sim \omega^{d-1}$.

To study the energy spectrum, we calculate the normal modes of a hard sphere colloidal crystal from the correlations in particle displacements. The colloidal particles used are small enough so that they perform small 'vibrations' in response to the thermal excitations of the surroundings. We use confocal microscopy to observe and record these particle motions in a two dimensional field of view. The eigenvalues of the dynamical matrix and normal modes are then obtained from the spatial correlations [5,11] of the measured displacements. The present experimental results are compared and complemented with a simplified continuum theory as well as Monte Carlo simulation of hard sphere crystals.

The main conclusion is that the spectrum of slice of a three dimensional system has a anomalous density of states which varies as $D(\omega) \sim \omega^3$. We explain this result with a simplified continuum theory; our conclusions contrast with those in [12].

Experiments and Analysis. Hard sphere colloidal systems undergo phase changes with the volume fraction ϕ as control parameter. There is no liquid-gas transition, but fluid-solid coexistence [1,2] is observed from the freezing transition point $\phi_f = 0.494$ until the melting point $\phi_m = 0.545$. A stable crystalline phase exists above 0.545 until the closed packed density at $\phi = 0.74$. The colloids we use are charge stabilized PMMA particles with a diameter of $a = 1.3\mu m$ with a very small size polydispersity of about 2%. The particles are dyed with rhodamine and are suspended in a CHB (cyclohexyl bromide) / decalin mixture which closely matches both the density and the index

Antina Ghosh 1, Romain Mari2, V.K. Chikkadi1, P.Schall1, A.C.Maggs3, D.Bonn1,4

of refraction of the particles. The crystal was grown in a sample cell made of parallel plates with a confinement of approximately $\sim 1mm$ along the vertical direction. The volume fraction of the present colloidal crystal is about $\phi \approx 0.57$. Using confocal microscopy we acquire images at a speed of 25 frames per second of a two dimensional section of about 60 μm x 60 μm of the larger three dimensional crystal. The entire crystal is polycrystalline, but we take our data from a region of the crystal that as far as we can see is perfectly crystalline and contains no defects. The particle positions are identified and tracked for a period of about 120 seconds using standard particle-tracking software; this results in a total of 3000 frames. Fig. 1 shows a typical snapshot of a two dimensional section of the measured crystal.
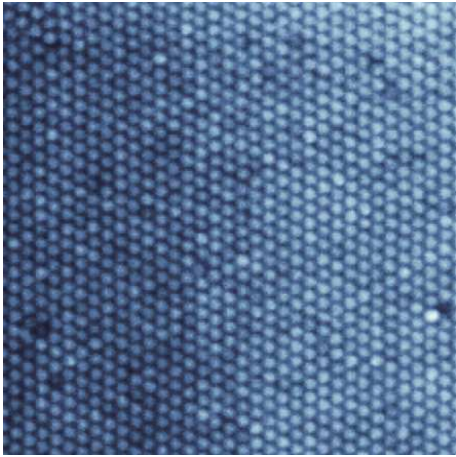

Fig. 1: Snapshot of a two dimensional section in a field of view of $60\mu m \times 60\mu m$ with a hexagonal symmetry.

We obtain an ensemble of projected particle positions $\bar{r}_i = \{x_i, y_i\}$ from the above measurements. The displacements from the mean position for the ith particle $\bar{u}(i) = \{u_x(i), u_y(i)\}$, where

$$u_\mu(i) = r_{\mu i} - \langle r_{\mu i} \rangle \qquad (1)$$

where "$\langle \rangle$" indicates an ensemble average. Now, the potential energy of a harmonic crystal can be written as,

$$U = 1/2 \sum_{\bar{k}} (u_\mu^*(\bar{k}) K_{\mu\nu}(k) u_\nu(\bar{k})), \qquad (2)$$

where $K_{\mu\nu}(k)$ [5] is the dynamical matrix in Fourier space and $u_\mu(\bar{k})$ is the Fourier transform of the displacement field. From equipartition each of the above quadratic terms $u_\mu^*(\bar{k}) K_{\mu\nu}(\bar{k}) u_\nu(\bar{k})/2$ contains an energy of $k_B T/2$. Therefore:

$$K_{\mu\nu}^{-1}(\bar{k}) = \langle \bar{u}_\mu^*(\bar{k}) \bar{u}_\nu(\bar{k}) \rangle / k_B T. \qquad (3)$$

The central question addressed in this paper is what happens if one tries to study the matrix eq. (3) using only a subset of the particles of the true three dimensional system, in particular if one reconstructs the dynamical matrix from measurements from a single plane within the sample. What is the nature of the effective interactions found in the analysis and what is the density of states found in the low dimensional slice?

We thus take our two-dimensional data and analyse it according to the above scheme to find an approximation to the matrix K^{-1}. In order to compare with the eigenmodes of a "hard" crystal (where the dynamics is underdamped) we define the mode frequencies [1] $\omega(\bar{k})$ from the eigenvalues λ of the matrix $K_{\mu\nu}(\bar{k})$ as,

$$\omega(\bar{k}) = \sqrt{1/\lambda(\bar{k})}. \qquad (4)$$

The density of normal modes $D(\omega)$ obtained from the above frequencies is shown in Fig. 2. A two peak structure is apparent in the density of states. Such peaks are familiar from the theory of lattice dynamics and often signal van Hove singularities [10] occurring due to the vanishing group velocities $\nabla_{\bar{k}}\omega$ at certain wave vectors. Indeed we see that the frequencies where $d\omega/dk \approx 0$ (close the zone boundary) on the dispersion curves coincide with the ones around which peaks appear in the density of states.

The important question is then how the measured density of states of the colloidal crystal compares to the integrated density of states $N(\omega) \sim \omega^3$ known from Debije theory. In the bottom panel of Fig. (2) we fit the integrated density of states to a power law with adjustable exponent, α. Our data best fits a value of $\alpha = 3.92$, far from the expected value $\alpha = 3$ for a three dimensional elastic medium and even further from the value $\alpha = 2$ expected in two dimensions. Given the surprising value for this exponent we decided to reanalyze our data using weaker assumptions on the form of the eigenfunctions- several artefacts seem plausible which could modify or overwhelm the expected density of states. Among these we can cite missing particles in the reconstruction (due to particle tracking errors), ambiguity in the choice of wavevectors and boundary conditions imposed in the imaged region (which is smaller than the sample size) and finally heterogeneity due to small differences between the particles making up the sample. We thus decided to implement a numerically slower but fuller analysis to see whether the conclusion is robust.

To be able to visualize the eigenmodes of the system we compute the spatial correlation between the particles in real space via the covariance matrix. This matrix, which has been used recently in studying normal mode properties of colloidal [5, 11–14] and granular systems [15], is defined as:

$$Q_{\mu\nu}(i,j) = \langle u_\mu(i) u_\nu(j) \rangle. \qquad (5)$$

This is a $2N \times 2N$ dimensional matrix with N particles. Any eigenvector $\{v_l\}$ of the above matrix represents a nor-

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[1]These are clearly not the frequencies of relaxation in the system, the calculation of which requires a study of the two-fluid hydrodynamics of the whole suspension.

a

b

c

Fig. 3: Tomography of the normal modes. The pictures from top to bottom correspond to increasing frequencies. The very low frequency ones show the extended plane wave nature of the modes. This coherent character is lost and modes appears to be random as higher frequencies are approached.
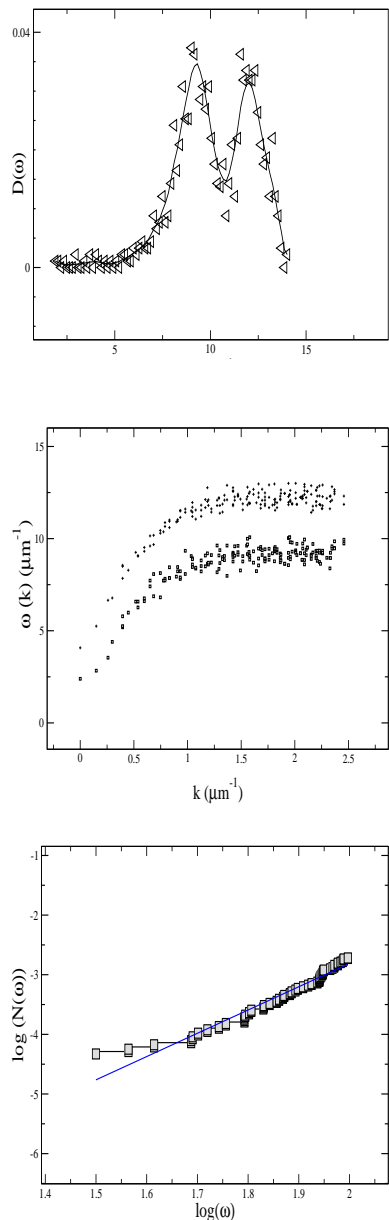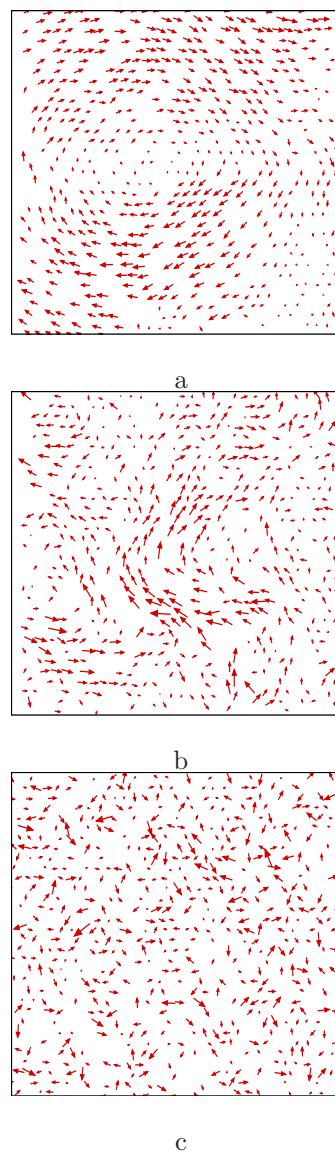
Fig. 2: Top: Density of states as obtained from the correlations, eq. 3. Center: The dispersion curves of transverse and longitudinal vibrations. The frequencies (vertical axis) near the zone boundary where $d\omega/dk \approx 0$ coincide with the positions of the singularities (peaks) in the density of states on top. Bottom: A power-law fit to the low frequency part of the cumulative density of states $N(\omega)$. The measured exponent ($N(\omega) \sim \omega^\alpha$), is $\alpha \approx 3.93 \pm 0.19$.

mal mode at a single "frequency" $w_l = \sqrt{1/\lambda_l}$. In our colloidal system, it allows us to *compute* the normal modes, rather than supposing plane waves as in eq. (3). A few examples of the normal modes are shown in Fig. (3). The modes in the low-frequency part of the spectrum show a clearly coherent motion extending over large part of the field of view. For higher frequencies the modes appears to be more random in nature.

To establish the correspondence between the above spatial correlation matrix with one calculated in Fourier space, we compute the matrix, $\tilde{Q}_{\mu\nu}(\bar{k}, \bar{k}') = \langle u_\mu^*(\bar{k}) u_\nu(\bar{k}') \rangle$. The diagonal blocks of $\tilde{Q}$ correspond to K^{-1} but away from the diagonal the elements in $(\bar{k}, \bar{k}')$ encode information about the heterogeneity and imperfections in the sample. If the distribution of eigenvalues found assuming translational invariance, and using the general form $\tilde{Q}$ are similar, we can have some hope that the data are not corrupted by noise, the choice of the boundary conditions or imperfections of the crystal.

Fig. 4 compares the density of states for both methods: they nearly fall on top of each other. Note also that

Antina Ghosh 1, Romain Mari2, V.K. Chikkadi1, P.Schall1, A.C.Maggs3, D.Bonn1,4

the finite resolution in the particle positions sets an upper limit on the 'frequency' scale of $\sim 34 nm$ [13] beyond which the frequencies can not be distinguished from the noise – for a detailed discussion see [14]. We also note that the van Hove peaks are weaker in this form of the analysis than in the purely Fourier based study. We interpret this as perhaps being due to the difficulty of combining the wave-vectors imposed by a square sample of size L with $k_\mu = 2\pi n/L$ with the geometry of the reciprocal space of a hexagonal lattice. However the exponent describing the the low frequency Debije regime is still very high $\alpha = 3.66 \pm 0.07$, where the error is that obtained from the fitting of the power-law exponent.
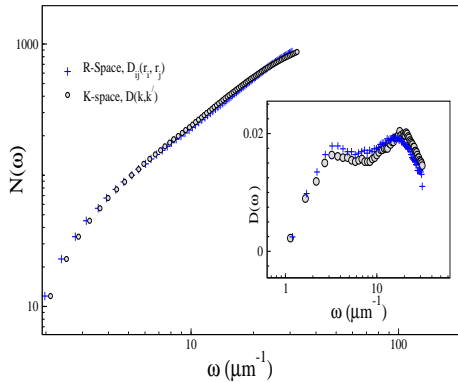

Fig. 4: Top: Normal mode spectrum: Cumulative and the Density of states for the present crystal as obtained from covariance matrix $Q_{\mu\nu}(\bar{r}_i, \bar{r}_j)$ in real space and its equivalent $\bar{Q}(k, k')$ in Fourier space. In the case of a perfect crystal these two methods should give identical results. In the case of imperfections the modes $|k\rangle$ and $|k'\rangle$ are no-longer orthonormal leading to differences in the spectra.

Theory and Simulation. The reliability of the experimental data has been tested using Monte-Carlo simulation of a hard sphere crystal. We use a face-centered cubic crystal made of 864 particles, with periodic boundary conditions. We thermally equilibrate the system over a sufficient number (10^6) of MC steps. We compute the covariance matrix (Eq. 5) to find the eigenmodes of the system along runs of 10^5 MC sweeps, out of which we use 5×10^4 snapshots for time averaging. We obtain this matrix for both the whole three dimensional system and two dimensional (111) planes, in order to mimic experimental conditions. As the number of particles (and thus modes) in a two dimensional plane is quite small, we average over several planes. The density of states we obtain is shown in Fig. 5. For the low frequency part of the cumulative DOS of the two dimensional slice we again find a density of states $N(\omega) \sim \omega^4$, which is compatibile with the experimental data, even if the limited system size excludes a detailed numerical fit. Certainly the density of states is falling off too fast for normal Debije behavior.
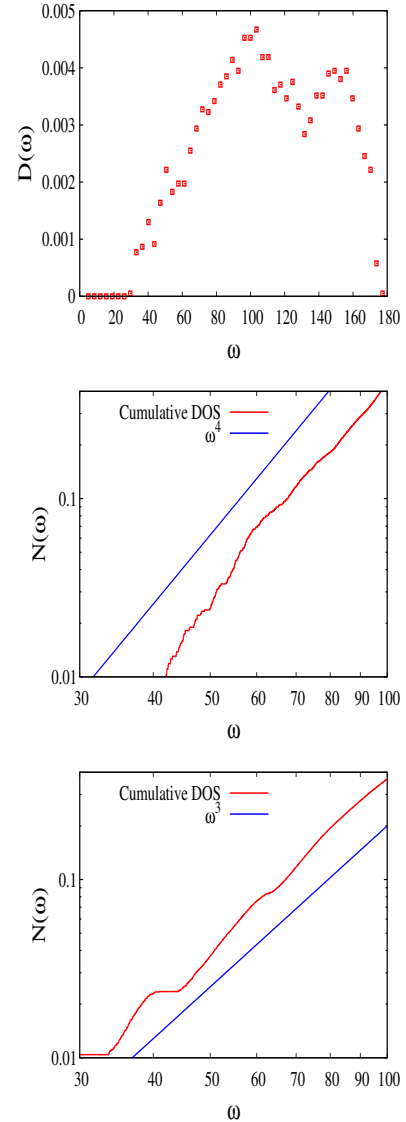
We now turn to a simple scalar theory which gives an

Fig. 5: Top: Density of states for a two dimensional hard sphere crystal from Monte-Carlo Simulations. Center: Low frequency part of the cumulative DOS for two dimensional slices of the three dimensional system, with logarithmic scale, showing a power-law behavior compatible with the Debije behavior $N(\omega) \sim \omega^4$. Bottom: As a comparison, low frequency part of the cumulative DOS for the whole three dimensional system, with logarithmic scale. Here, the behavior is compatible with the three dimensional Debije law $N(\omega) \sim \omega^3$. Frequencies are in unit of the inverse particle diameter.

indication how Debije theory must be modified when one observes two dimensional cuts of a three dimensional sample. A theory based on full three dimensional elasticity is also possible but we leave this to a later publication. We consider fluctuations of a scalar quantity u with an energy which is of the form

$$U = \frac{A}{2} \int (\text{grad } u)^2 \, \mathrm{d}^3\mathbf{r} \qquad (6)$$

A is an elastic modulus. In the generalization to elastic fluctuations one would consider an energy based on the symmetrized strain tensor. In Fourier space the energy has the form

$$U = \frac{A}{2} \sum_{\bar{k}} k^2 |u_{\bar{k}}^2| \qquad (7)$$

we notice the usual scaling of the elastic energy in k^2.

In an under-damped system with kinetic energy $\rho \dot{u}^2/2$ this gives rise to the dispersion relation $\omega^2 = c^2 k^2$. One thus expects a density of states

$$dN \sim k^2 \, dk \sim \omega^2 d\omega \qquad (8)$$

It is this scaling of the density of states in ω^2 that is known from the theory of Debije.

In a three dimensional sample thermal fluctuations excite the system, so that equipartition and eq. (7) implies

$$\langle |u_{\bar{k}}|^2 \rangle = \frac{k_B T}{A k^2} \qquad (9)$$

This gives a decay of correlations in real space which is given by the inverse Fourier transform of $1/k^2$. We can find the result immediately by reference to electrostatics:

$$\langle u(i) u(j) \rangle = \frac{1}{4\pi A |\bar{r}_i - \bar{r}_j|} \qquad (10)$$

a Coulomb like decay of correlations.

Now take a two dimensional slice of the system. Within this slice the correlations are still decaying as $1/r$. We wish to describe what we see, however, in terms of a purely two-dimensional theory, so we perform a two dimensional Fourier transform to find the effective stiffness. Thus

$$\langle |u_{\bar{k}}|^2 \rangle_2 = \int \frac{1}{Ar} e^{i\bar{k}_2 \cdot \bar{r}} d^2 \bar{r} = \frac{1}{2A|\bar{k}_2|} \qquad (11)$$

where we use the subscript 2 to indicate that we are working with the two-dimensional projected objects. The result is rather interesting: rather than correlations in three dimensional being described by a decay in $1/k^2$ we find a slower decay: $1/|k_2|$.

Now that we have the scaling form of the correlations we can work backwards and deduce the effective elastic theory in two dimensions

$$U_2 = \frac{A}{2} \sum_{\bar{k}_2} 2|\bar{k}_2| |u_{\bar{k}_2}|_2^2 \qquad (12)$$

Thus the elastic behavior in real space corresponds to fractional derivatives of the field u leading to long-ranged effective interactions in the projected system.

We now calculate the "propagative" eigenvalue by defining

$$\omega_2^2 = 2A|\bar{k}_2| \qquad (13)$$

which is the analogy of $\omega^2 = c^2 k^2$ that we use in three dimensions. We note that the dispersion law is very different from that of usual elastic problems. The density of

states of this two dimensional matrix are just

$$dN_2 \sim k_2 dk_2 \sim \frac{\omega_2^3}{A^2} d\omega_2 \qquad (14)$$

The density of states is thus $D(\omega) \sim \omega_2^3$ and the integrated density of the states $N(\omega) \sim \omega_2^4$, in good agreement with what was found in the experiment and in the simulations.

Conclusions. We have studied the dynamics of a hard sphere colloidal crystal at a volume fraction $\phi \sim 0.57$, a volume fraction slightly above the melting transition using confocal microscopy. The density of states and normal modes were obtained from measured particle displacements. Hard sphere systems are usually weakly connected and the interaction potential is strongly anharmonic, however we show that the density of states can be understood using continuum elasticity theory

The effective exponent for the frequency-dependence of the density of states was measured in the low energy regime and is inconsistent with the expected Debije behavior in $D(\omega) \sim \omega^{d-1}$ for both $d = 2$ and $d = 3$. We found that the data can be explained by a theory with an unusual energy dispersion relation in $|\bar{k}_2|$, which gives $D(\omega) \sim \omega^3$. This expression agrees with both the experiments and the simulations. It is interesting to note that the same energy function was found in [16] where the spreading of a droplet was expressed as the effective dynamics of a contact line. Again we are in the presence of a physical system projected to lower dimensions.

REFERENCES

[1] Pusey P. N. and van Megen W., *Nature* , **320** (1986) 340.
[2] Rintoul M. D. and Torquato S., *Phys. Rev. Lett.* , **77** (1996) 4198.
[3] Aastuen D. J. W., Clark N. A., Cotter L. K. and Ackerson B. J., *Phys. Rev. Lett.* , **57** (1986) 1733.
[4] Pusey P. N. and van Megen W., *Nature* , **320** (1986) 340.
[5] Keim P., Maret G., Herz U. and von Grünberg H. H., *Phys. Rev. Lett.* , **92** (2004) 215504.
[6] Zahn K., Wille A., Maret G., Sengupta S. and Nielaba P., *Phys. Rev. Lett.* , **90** (2003) 155506.
[7] Sirota E. B., Ou-Yang H. D., Sinha S. K., Chaikin P. M., Axe J. D. and Fujii Y., *Phys. Rev. Lett.* , **62** (1989) 1524.
[8] Cheng Z., Zhu J., Russel W. B. and Chaikin P. M., *Phys. Rev. Lett.* , **85** (2000) 1460.
[9] Penciu R. S., Kafesaki M., Fytas G., Economou E. N., Steffen W., Hollingsworth A. and Russel W. B., *EPL (Europhysics Letters)* , **58** (2002) 699.
[10] Ghatak A. K. and Kothari L. S., *An Introduction to Lattice Dynamics* (Addison-Wesley, New York) 1972.
[11] Ghosh A., Chikkadi V. K., Schall P., Kurchan J. and Bonn D., *Phys. Rev. Lett.* , **104** (2010) 248305.

Antina Ghosh 1, Romain Mari2, V.K. Chikkadi1, P.Schall1, A.C.Maggs3, D.Bonn1,4

[12] Kaya D., Green N. L., Maloney C. E. and Islam M. F., *Science* , **329** (2010) 656.

[13] Chen K., Ellenbroek W. G., Zhang Z., Chen D. T. N., Yunker P. J., Henkes S., Brito C., Dauchot O., van Saarloos W., Liu A. J. and Yodh A. G., *Phys. Rev. Lett.* , **105** (2010) 025501.

[14] Ghosh A., Mari R., Chikkadi V., Schall P., Kurchan J. and Bonn D., *Soft Matter* , **6** (2010) 3082.

[15] Brito C., Dauchot O., Biroli G. and Bouchaud J.-P., *Soft Matter* , **6** (2010) 3013.

[16] Joanny J. F. and de Gennes P. G., *J. Chem. Phys.* , **81** (1984) 552.