Comment on "Evidence of Many-Particle Interactions in Two-Dimensional Charge-Stabilized Colloidal Crystals"

In a recent Letter, Dyshlovenko reported on a numerical study of the electrostatic interaction in two-dimensional colloidal crystals obeying the nonlinear Poisson-Boltzmann equation [1]. From the calculated force constants of the crystal he concluded that the contribution of many-particle interactions is significant for the total electrostatic interactions. However, his analysis assumes implicitly that the pressure in the crystals is zero, which is not the case in charge-stabilized crystals. In addition to this remark I show in this Comment that the symmetry of the hexagonal lattice, which was used in Ref. [1], makes it very difficult to reveal the significance of many-particle interactions by an analysis of force constants.

If the interaction ϕ between particle α and β is given by a pair-potential with radial symmetry, the total potential energy of the many-particle system is given by $V = \frac{1}{2}\sum_{\alpha \neq \beta}\phi(|\mathbf{r}^\alpha - \mathbf{r}^\beta|)$. The force constants are defined by $C_{ik}^{\alpha\beta} = \frac{\partial^2 V}{\partial R_i^\alpha \partial R_k^{\alpha+\beta}}$, where $\mathbf{R}^\alpha$ denotes the reference lattice position of particle α and the subscripts i, k indicate Cartesian components. From the potential energy the force constants between particle α and β can be calculated directly

$$C_{ik}^{\alpha\beta} = -\frac{(R_i^\alpha - R_i^\beta)(R_k^\alpha - R_k^\beta)}{R_{\alpha\beta}^2}\left[\phi'' - \frac{\phi'}{R_{\alpha\beta}}\right] - \frac{\phi'}{R_{\alpha\beta}}\delta_{ik}.$$

ϕ' and ϕ'' are the radial derivatives of the pair-potential evaluated at the distance $R_{\alpha\beta}$ between particle α and β. In the following, the coordinate system and the indexing of the particles is as in Fig. 1 of Ref. [1]. With the expression for $C_{ik}^{\alpha\beta}$ the matrix of force constants between the particle 0 and the first order neighbor particle (nearest neighbor) 1 of the hexagonal crystal with lattice constant a can be constructed

$$C^{(1,0)} = -\begin{pmatrix} \phi''(a) & 0 \\ 0 & \frac{\phi'(a)}{a} \end{pmatrix}. \tag{1}$$

This matrix was not correctly calculated in Ref. [1] (Eq. 7b); the element $C_{yy}^{(1,0)}$ was taken to be zero instead of $\phi'(a)/a$. This term accounts for the external pressure in the system necessary for the stability of the colloidal crystal [2].

Dyshlovenko derived the force constants of hexagonal charge-stabilized colloidal crystals by numerically solving the nonlinear Poisson-Boltzmann equation. This resulted in nonzero matrix elements $C_{yy}^{(1,0)}$. He assumed that this

observation is a fingerprint of many-body effects. Furthermore, he used $C_{yy}^{(1,0)}$ as a quantitative measure of these effects. However, $C_{yy}^{(1,0)}$ is related to the pressure of the system and thus Dyshlovenko's interpretation of the force constants is not correct.

Moreover, the high symmetry of the hexagonal lattice makes it impossible to draw any information on the nature of the interactions from measured or calculated force constants: As the matrices of force constants are symmetric [see Eq. (6) in Ref. [1]] and as the hexagonal lattice is invariant under a reflection at the x axis of the coordinate system the matrix of force constants between particle 0 and 1 is diagonal. Thus $C^{(1,0)}$ is given in its most general form by two parameters A and B:

$$C^{(1,0)} = -\begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix}. \tag{2}$$

The five other first order matrices can be calculated using the sixfold rotational symmetry of the lattice. Therefore, all these matrices can be expressed in terms of A and B. This means, solely A and B can be derived from measured or calculated first order matrices, whatever the interaction in the system is. From a comparison of Eqs. (1) and (2) it becomes evident that (A, B) can always be interpreted as $[\phi''(a), \phi'(a)/a]$ irrespective of the true interaction.

As analogous symmetry considerations can be performed for second and third order matrices of force constants they also depend on two parameters which are interpretable as $\phi''(d)$ and $\phi'(d)/d$ at the corresponding distance d. Only fourth and higher order matrices depend on more then two parameters and therefore allow to study the significance of many-particle effects.

Thus it is very difficult to reveal many-particle interactions in hexagonal charge-stabilized crystals by an analysis of force constants, since force constants at large distances need to be determined.

The author of Ref. [1] agrees with the arguments of this comment.

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