Elastic properties of static charge-stabilized colloidal crystal with two-dimensional hexagonal lattice

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Abstract. Two-dimensional charge-stabilized colloidal crystal with a hexagonal crystal lattice and constant electric potential on the particles is studied numerically. The properties of the crystal are described by the theory based on the Poisson-Boltzmann non-linear differential equation. The force constants and the equilibrium pressure in the crystals are calculated for a broad range of the lattice parameters. The numerical procedures of the force constant and pressure determination is briefly described. Elastic constants of the first and second order are also calculated on the base of the force constants to obtain information about the many-body effective interactions in the system. It was shown that the Cauchy relation between the elastic constants breaks down in the whole range of the lattice parameter especially at higher densities. This can be interpreted as an effect of the many-body effective interaction between the particles in the crystal.

1. Introduction

Colloidal crystals are dispersions of macroscopic colloidal particles arranged into a regular crystalline lattice. They play an increasingly important role as a basis for the development of novel materials, in particular, in photonic crystal manufacture [1, 2, 3]. They are also a well-defined model systems resembling behavior of conventional crystals, whose properties, however, are much easier to control and observe. In charge-stabilized colloidal crystal, the particles are electrically charged and immersed into a liquid electrolyte.

In the present paper, we study numerically the two-dimensional charge-stabilized colloidal crystal obeying the general non-linear Poisson-Boltzmann (PB) equation making no a priori assumptions about the properties of the inter-particle interaction. Within the framework of the theory based on the PB equation, we calculate the force constants and equilibrium pressure in the system as well as elastic constants. Analysis of the elastic constants provides some information about the possible presence of the many-body interactions in the system. If each pair of the particles in a regular crystal lattice interacts via a central pair potential, then the elastic constants must satisfy the Cauchy relations. Violation of the Cauchy relations means that the total energy of the crystal cannot be represented as a sum of pair contributions of such kind and that the many-body effective interactions can play some role in the system. It is shown in the paper that this is the case for the crystal studied.
2. Model and governing equations

Colloidal crystal under consideration consists of circular colloidal particles of radius $R$ arranged in a two-dimensional hexagonal lattice with the lattice constant $a$. Alternatively, the particles can be treated as infinitely long uniform cylinders in three dimensions. The system of the particles is immersed in a binary symmetrical univalent electrolyte (1:1 electrolyte). The particles are electrically charged rigid dielectric bodies. Electric potential $\phi_0$ at the surface of the particles is kept constant (the so-called constant-potential or cp model).

We assume that the charge-stabilized colloidal system obeys the non-linear PB equation [4, 5] for the electric potential $\phi$. The PB equation for the 1:1 electrolyte has the form

$$\nabla^2 \phi = \frac{q_e n}{\epsilon \epsilon_0} \left[ \exp \left( -\frac{q_e \phi}{k_B T} \right) - \exp \left( \frac{q_e \phi}{k_B T} \right) \right]$$

(1)

in the rationalized SI unit system. This equation is valid in the electrolyte domain outside the particles. Here $n$ is the bulk number concentration of either species of the electrolyte, $q_e$ is the elementary charge, $\epsilon$ is the relative dielectric permittivity of the electrolyte, $\epsilon_0$ is the electric constant, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature.

To benefit from the dimensionless form of the governing equations and boundary conditions we introduce units $\kappa^{-1} = (2nq_e^2/\epsilon \epsilon_0 k_B T)^{-1/2}$ (Debye length) and $k_B T/q_e$ for length and electrostatic potential respectively. From here on all the variables are thought to be dimensionless. The dimensionless equation for our system can then be written as

$$\nabla^2 \phi = \sinh \phi$$

(2)

Electric field at the particle-electrolyte interface meets simple Dirichlet boundary condition

$$\phi = \phi_0,$$

(3)

where $\phi_0 = \text{const}$ is a potential at the particles. Electric field inside the particles is equal to zero.

Domain of the problem for numerical solution consists of the Wigner-Seitz cells of the arbitrarily chosen central particle 0 and its 18 nearest neighbours of order 1 to 3. Interior of the particles is excluded from the domain. The central particle can be shifted slightly from its equilibrium position in different spatial configurations during the numerical experiments. Equilibrium position of a particle is given by vector $M = m_1 a_1 + m_2 a_2$ where $m_1$ and $m_2$ are integer numbers and $a_1$ and $a_2$ are the primitive vectors of the lattice ($a_1$ is parallel to the $x$-axis and $a_2$ is directed at angle $\pi/3$ relative to $a_1$).

The homogeneous Neumann boundary condition

$$\nabla \phi \cdot n = 0,$$

(4)

where $n$ is an outer unit normal, holds at the outer boundary of the domain. This means the normal component of the electric field is equal to zero at the external boundary.

Differential equation (2) with boundary conditions (3) and (4) constitute a boundary problem on the domain described above. Solution $\phi = \phi(x, y)$ of this problem fully determine the properties of the system. Calculation of both the forces and pressure is based on the stress tensor $T$ of the PB equation:

$$T = \nabla \phi \otimes \nabla \phi - \left( \frac{1}{2} \nabla \phi^2 + \cosh \phi - 1 \right) I,$$

(5)

where $I$ is an identity matrix.

Numerical solution was carried out by the finite-element method. Calculations were partly supported by the Supercomputing Center of Lomonosov Moscow State University [6].
3. Force constants

Force constants $C_{\alpha\beta}^M$ of a two-dimensional monatomic crystal are defined by the following expression [7]:

$$C_{\alpha\beta}^M = \frac{\partial^2 U}{\partial Z_{\alpha,N} \partial Z_{\beta,N+M}},$$

(6)

where $U$ is the (free) energy of the system, $Z_{\alpha,N}$ is an $\alpha$-component of the displacement $Z$ of the particle pointed by vector $N$ from its equilibrium position, $\alpha = x, y$, $\beta = x, y$, $N$ and $M$ are vectors of the Bravais lattice. Since force constants do not depend on vector $N$ due to the translational symmetry of potential energy $U$, one can set $N = 0$ without loss of generality. Force constants for any particular $M$ can be arranged into a square $2 \times 2$ matrix $C^M = \|C_{\alpha\beta}^M\|$.

Derivative

$$F_{\alpha,M} = -\frac{\partial U}{\partial Z_{\alpha,M}},$$

(7)

is the $\alpha$-component $F_{\alpha,M}$ of the force on the particle $M$. Then the force constant

$$C_{\alpha\beta}^M = -\frac{\partial F_{\alpha,M}}{\partial Z_{\beta,0}}.$$  

(8)

The force component $F_{\alpha,M}$ can be calculated directly, without differentiation, by integrating the stress tensor (5):

$$F_{\alpha,N} = \oint_{\Gamma} \mathbf{e}_\alpha \cdot T \cdot \mathbf{n} \, dl,$$

(9)

where $L$ is the length of the Wigner-Seitz cell’s boundary $\Gamma$, $\mathbf{n}$ is an outer unit normal to the element length $dl$, and $\mathbf{e}_\alpha$ is a corresponding unit basis vector of the Cartesian coordinate system.

The functional dependences $F_{\alpha,M}(Z_{\beta,0})$, $\beta = x, y$ for each $\alpha$ and $M$ in the domain were determined for a set of 21 equally spaced values of $Z_{\beta,0}$ comprising of zero value, ten steps in the positive $\beta$-direction, and ten of the same steps in the negative $\beta$-direction. The largest shift of particle 0 from its equilibrium position amounted to 10% of the separation distance $(a - 2R)$ between the neatest particles. Numerical calculations were actually carried out only for positive displacements. The data for negative displacements were obtained from the data for positive ones with the help of inversion symmetry.

To find the force constants, the functions $F_{\alpha,M}(X)$ for all vectors $M$ and $\alpha = x, y$ with $X = Z_{\beta,0}$, $\beta = x, y$, were fitted with polynomials:

$$F_{\alpha,M}(X) = a_0 + a_1 X + a_2 X^2 + \ldots + a_n X^n,$$

(10)

The best fitting was obtained with $n = 3$. Then $C_{\alpha\beta}^M = -a_1$.

The amount of calculation can be significantly reduced taking into account the point symmetry of a particular crystal. For the hexagonal lattice, it is sufficient [8] to make shift of the central particle only in positive $x$-direction, while the $y$-directional shifts can be avoided. Moreover, only an (upper) half of the domain can be used since the crystal retains the mirror symmetry relative the $x$-axis during the $x$-shifts. If the force constant matrix $C^M$ of particle $M$ is known, then the matrix $C^{M'}$ of nearest neighbour $M'$ of the same order can be found from the following relation:

$$C^{M'} = R^T(\theta) C^M R(\theta).$$

(11)

Here $\theta$ is the angle of rotation from $M$ to $M'$. Matrix $R(\theta)$ is a matrix of rotation through the angle $\theta$, and superscript $T$ means matrix transposition. For that reason, the minimal set of
data for the force constants can include only matrices $C^{(1, 0)}$, $C^{(-1, 2)}$ and $C^{(2, 0)}$ which are all diagonal.

Numerical results for the force constants at $R = 1$ and $\phi_0 = 2$ are shown in Figs. 1 to 4. The scales of the vertical axes are very different in the figures. The curves for nearest neighbours of higher orders are rather noisy. For the neighbours of the 3rd order, the force constants are hardly resolved in our calculations and the results give only the order of magnitude. Behavior of the force constants for the large lattice parameters is close to exponential. In contrast to the crystal with constant charge density on the particles [8], the curves do not rise monotonically while the lattice parameter decreases. There are definite extrema on the curves so that the rigidity of the crystal decreases at high densities.

4. Elastic constants

Elastic constants describe macroscopic elasticity of the whole piece of matter. Elastic constants of the second order $C_{\alpha\beta\sigma\tau}$ appear in a series expansion of the strain-energy density with respect to the Lagrangian finite strain tensor components $\eta_{\alpha\beta}$ [9]. An alternative set of elastic constants
arises from expansion with respect to infinitesimal strain tensor components $\epsilon_{\alpha\beta}$. There are only three nontrivial second-order elastic constants $C_{\alpha\beta\sigma\tau}$ for the hexagonal lattice, $C_{xxxx}$, $C_{xxyy}$, $C_{xyxy}$. The two sets of elastic constants are related to each other by the following expressions: $C_{xxxx} = B_{xxxx} + p$, $C_{xxyy} = B_{xxyy} - p$, $C_{xyxy} = B_{xyxy} + p$, where $p$ is the pressure (more precisely, the excess of the equilibrium osmotic pressure over the pressure in the bulk).

Elastic constants can be expressed via the force constants according to the theory of elasticity of the solid under stress [10]. Pressure $p$ is calculated through the stress tensor (5) by averaging the normal component of the force on the boundary of the Wigner-Seitz cell [11]:

$$p = -\frac{1}{L} \oint_{\Gamma} \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} \, dl,$$

where $L$ is the length of the Wigner-Seitz cell’s boundary $\Gamma$. The integration in (12) is made for the colloidal particle located in its equilibrium position. Numerical results for the elastic constants for $R = 1$ and $\phi_0 = 2$ are shown in Fig. 5 and Fig. 6.

Figure 5. Equilibrium pressure (elastic constant of the 1st order).

Figure 6. Elastic constants of the 2nd order $B_{ijkl}$.

Within the one-component model [12] the interaction in a colloidal system is reduced to the effective interaction between the colloidal particles only. If this interaction is central pairwise then Cauchy relations between the elastic constants holds additionally [9]. In the case of two-dimensional hexagonal lattice, there is only one such relation:

$$C_{1122} = C_{1212}.$$  

The ratio $C_{1122}/C_{1212}$ of the two constants is shown in Fig. 7

It is seen from Fig. 7 that there is a noticeable deviation of ratio $C_{1122}/C_{1212}$ from unit in the whole region of the lattice parameter except possibly for very large separation distances. Effective interaction is close to be pairwise only at a low density of the system where the interaction itself is very weak. The deviation from the Cauchy relation grows monotonically while the density rises up to the almost contact between the particles. Relation $C_{1122} < C_{1212}$ holds for any values of the lattice parameter. That means that many-body interactions play some role in the system and proper elastic constants cannot be obtained with pair central potential of any kind.
5. Conclusions

Two-dimensional charge-stabilized colloidal crystal with hexagonal crystal lattice and constant potential on the particles was studied numerically within the static lattice approximation. The system obeys the general non-linear Poisson-Boltzmann equation. Numerical procedure based on light disturbance of the system by shifting a single particle from its equilibrium position was proposed for determination of the force constants. Complete set of the force constants of the nearest neighbours up to the third order and equilibrium pressure were calculated for a broad range of lattice parameter of the crystal.

Elastic constants of the first and second order were also calculated and used to verify the validity of the Cauchy relation \( C_{1122} = C_{1212} \). Significant deviation from the Cauchy relation was observed that proves the presence of many-body interactions in the system. Further calculations are needed for quantitative estimation of many-body contributions into the total interparticle interaction.

References

[1] Tarhan I I and Watson G H 1996 Phys. Rev. Lett. 76 315
[2] van Blaaderen A, Ruel R and Wiltzius P 1997 Nature 385 321
[3] Joannopoulos J D, Villeneuve P R and Fan S H 1997 Nature 386 143
[4] Israelachvili J N 1991 Intermolecular and Surface Forces (Academic Press) chapter 12
[5] Derjaguin B V, Churaev N V and Muller V M 1987 Poverkhnostnye Sily (Surface Forces) (Moscow: Nauka) (in Russian) chapter 1
[6] Sadovnichy V, Tikhonravov A, Voevodin V and Opanasenko V 2013 "Lomonosov": Supercomputing at Moscow State University. In Contemporary High Performance Computing: From Petascale toward Exascale (Chapman & Hall/CRC Computational Science) (Boca Raton, USA: CRC Press) pp 283-307
[7] Feynman R P 1972 Statistical Mechanics (Massachusetts: W. A. Benjamin) chapter 1
[8] Dyshlovenko P E 2007 Colloid J. 69 13
[9] Dyshlovenko P E 2007 Kolloidny Zhurnal 69 18 (Russian original)
[10] Barron T H K and Klein M L 1965 Proc. Phys. Soc. 85 523
[11] Wallace D C 1965 Rev. Mod. Phys. 37 57
[12] Belloni E 2000 J. Phys.: Condens. Matter. 12 R549