Calculation of the third-order elastic constants of charge-stabilized colloidal crystals with monatomic hexagonal crystal lattice

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Abstract. Elastic constants up to the third order of a charge-stabilized colloidal crystal with monatomic hexagonal crystal lattice are obtained numerically. The properties of the crystal are described by the Poisson-Boltzmann nonlinear differential equation for the electric potential. The elastic constants are obtained from the stress-strain relations for the crystal treated as a solid medium with an initial stress.

1. Introduction
Colloidal crystals are dispersions of solid particles in a liquid medium in which the particles are spatially ordered and form a crystal structure of a certain type. Interest in colloidal crystals has recently increased significantly due to the possibility of their use in creation of photonic crystals and self-assembling structures [1]. They can also serve as a model in study of conventional molecular crystals as well as disordered colloidal systems.

In charge stabilized colloidal crystals, the particles are electrically charged, while the liquid medium is usually an electrolyte. We describe a model crystal which is formed by electrically charged rigid disks arranged into a hexagonal crystal lattice and immersed into an electrolyte with two species of valences +1 and −1 (1:1 electrolyte). Electric potential in the electrolyte is described by the nonlinear Poisson-Boltzmann (PB) differential equation in its standard form [2]. It is appropriate for the systems with a 1:1 electrolyte, in which the correlation effects are rather small. Correlation effects that have been intensively studied over the past twenty years [3-9] may possibly be included in the model in the form of a modified Poisson-Boltzmann equation. The van der Waals forces are not included in the model to keep it simple and to keep track of the electrostatic contributions solely into the elastic properties of the crystal.

To calculate elastic constants, we treat the crystal as a solid medium with an initial stress [10]. External pressure in equilibrium is necessary here for stability of the crystal and is provided by the external boundaries. One can also consider closed areas like a drop [11]. An alternative mechanism of stabilization is described in [12].

We propose the numerical method and calculate elastic constants of the model crystal up to the third order. Elastic constants are derived from the stress-strain relations obtained numerically. We employ the relations between the second Piola-Kirchhoff stress tensor and the Lagrange strain tensor [13]. Elastic constants up to the second order for this crystal were obtained earlier in [14] by an alternative method. We compare both sets of the results.
2. Description of the Model

The unit cell of the crystal is shown in the figure 1(a). The model has three parameters: the lattice parameter $a$ and the radius of the particles $R$ and the surface charge density on the particles $\sigma_0$.

![Figure 1](image)

**Figure 1.** The unit cell of the hexagonal crystal with a circular particle at the centre (a) and domain for the numerical calculations (b). Under strain, both the cell and domain are deformed accordingly. Symbols are described in the text.

Electric potential $\phi$ in the electrolyte at the absolute temperature $T$ with the bulk concentration of the species $n_0$ and the relative dielectric permittivity $\varepsilon$ obeys the PB equation

$$\nabla^2 \phi = \frac{2q_e n_0}{\varepsilon_0 \varepsilon} \sinh \left( \frac{q_e \phi}{kT} \right).$$

(1)

Using the Debye length $\kappa^{-1} = \left( 2n_0 q_e^2 / \varepsilon_0 \varepsilon kT \right)^{-1/2}$ as a distance unit and expression $kT/q_e$ for the electric potential, one can reduce the equation (1) to its dimensionless form

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

(2)

The dimensionless quantities which are convenient for computer calculations are only used hereafter in the present paper.

We assume that the dielectric permittivity of the electrolyte is big and the approximation of the infinite dielectric permittivity can be used. This is a good approximation for aqua solutions. Then, the domain of the problem includes only the electrolyte region and the following nonhomogeneous Neumann boundary conditions (dimensionless) hold on the surface of the particle:

$$-\nabla \phi \cdot \mathbf{n} = \sigma_0,$$

(3)

where $\mathbf{n}$ is an external unit normal vector of the particle. Electric potential inside the particle can be calculated separately if needed.

The domain for numerical calculations is shown in the figure 1(b). It is only a part of the whole unit cell. The straight external sides of the domain are all the mirror axes of the crystal. Thus the simple homogeneous Neumann boundary conditions hold on them:

$$-\nabla \phi \cdot \mathbf{n} = 0,$$

(4)

where $\mathbf{n}$ is an external unit normal vector of the domain. This is valid for the deformed configurations as well since only the stretching in $x$ and $y$ directions are used in the numerical experiments (see below).

Equations (2)–(4) together with the domain constitute the boundary value problem to be solved in any given spatial configuration.

3. Numerical Experiment
We define elastic constants from the following stress-strain relations [13]:
\[ \Sigma_{ij} = C_{ij} \delta_{ij} + C_{ijkl} \eta_{kl} + \frac{1}{2} C_{ijklmn} \eta_{lm} \eta_{mn} + \ldots, \] (5)
where dots designate cubic and higher order terms omitted, \( \Sigma_{ij} \) is the second Piola-Kirchhoff stress tensor, \( \eta_{kl} \) is the Lagrange strain tensor, \( C_{ij} \), \( C_{ijkl} \) and \( C_{ijklmn} \) are tensors of the elastic constants, \( \delta_{ij} \) is a Kronecker's delta-symbol. The subscripts go over the values 1, 2 that correspond to the x, y directions respectively and summation over repeating subscripts is implied. Elastic constants are symmetric with respect to the interchanges of subscripts in each pair as well as of different pairs of subscripts.

Some elastic constants are identically equal to zero while the non-zero constants are not fully independent due to the high symmetry of the hexagonal crystal lattice. The choice of independent non-zero constants is not unique. Our choice in the present paper is the following: one elastic constant of the first order, \( C_{11} \), two constants of the second order, \( C_{1111} \) and \( C_{1112} \), and three constants of the third order, \( C_{111111} \), \( C_{111112} \) and \( C_{222222} \). In the Voigt's notation they are \( C_1 \), \( C_{11} \), \( C_{12} \), \( C_{111} \), \( C_{112} \), \( C_{22} \) respectively. The rest non-zero constants can be expressed through the independent ones.

The independent elastic constants are obtained from the two series of deformation: stretching in \( x \)-direction (zig) and unibiaxial (bi) stretching in \( xy \)-plane. The first series gives two stress-strain relations
\[ \Sigma_{ij} = C_{ij} \eta_{ij} + \frac{1}{2} C_{ijkl} \eta_{ij} \eta_{kl} + \ldots, \] (6a)
\[ \Sigma_{ij} = C_{ij} \eta_{ij} + \frac{1}{2} C_{ijkl} \eta_{ij} \eta_{kl} + \ldots, \] (6b)
where \( \eta_1 \equiv \eta_1 \) is just a strain parameter. The second series gives
\[ \Sigma_{i1} = \Sigma_{21} = C_1 + \left( C_{11} + C_{12} \right) \eta_1 + \frac{1}{2} \left( 2C_{111} - C_{222} + 3C_{112} \right) \eta_1^2 + \ldots, \] (6c)
where \( \eta_1 \equiv \eta_1 = \eta_2 \).

The stress tensor \( \Sigma_{ij} \) (tensor notation) is related to the Cauchy stress tensor \( T_{ij} \) as follows:
\[ \Sigma_{ij} = J \gamma_{ij} \gamma_{jk} T_{kj}, \] (7)
where \( \gamma_{ij} \) are components of the tensor inverse to the deformation gradient tensor \( \alpha_{ij} \), \( J = \det(\alpha_{ij}) \), and \( \alpha_{ij} = \delta_{ij} + u_{ij} \), where \( u_{ij} \) is a displacement gradient. Since \( \eta_{ij} = 1/2 \left( u_{ij} + u_{ji} + u_{ij} u_{ji} \right) \), the only non-zero components of tensor \( u_{ij} \) are the following: \( u_{11} = -1 + \sqrt{1 + 2\eta_1} \) in the first experiment and \( u_{11} = u_{22} = -1 + \sqrt{1 + 2\eta_2} \) in the second one.

To calculate the Cauchy stress tensor \( T_{ij} \) we need some designations shown in the figure 1(a). The sides of the hexagon, both in the initial and deformed configurations, can be split into three pairs, \( S^{(m)} \), \( S^{(m)} \), \( m = 1, 2, 3 \). The opposite sides in each pair are separated by the corresponding vectors of elementary translations, \( r^{(m)} \), \( m = 1, 2, 3 \). These vectors for the initial configuration written in the Cartesian coordinate system are the following: \( r^{(1)} = \left( \frac{1}{2}, -\frac{\sqrt{3}}{2} \right) a \), \( r^{(2)} = (1, 0) a \), \( r^{(3)} = \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right) a \). In the deformed configurations, the vectors \( r^{(m)} \) are transformed according to the strain.

The Cauchy stress tensor \( T_{ik} \) in an arbitrary configuration is calculated then in the following way [15]:
\[ T_{ik} = \frac{1}{V} \sum_{m=1}^{3} r_{i}^{(m)} \int_{S^{(m)}} \Pi_{j} d\alpha_{j}, \] (8)
where integration is carried out over the sides $S^{(m)}$ pointed by the vectors $\mathbf{r}^{(m)}$, $\mathbf{l}_k^{(m)}$ are components of the vectors $\mathbf{r}^{(m)}$, $V_c$ is an area of the unit cell and $\Pi_{ij}$ is the stress tensor of the PB equation for the 1:1 electrolyte:

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

where $I$ is a unit tensor.

We obtain stress-strain relations (6) for the crystals with $R = 1$, $\sigma_0 = 2$ and the lattice parameter $a$ in the range 2.3 to 6.0. Strain parameter $\eta$ in (6) varies from $-0.1$ to $+0.1$ with step 0.001. Polynomial approximation of the experimental stress-strain curves give the elastic constants.

The boundary value problem for any given set of parameters $R$, $\sigma_0$, $a$ and $\eta$ is solved by the finite element method with triangular free meshes and quadratic Lagrangian finite elements. Calculations were supported by the Supercomputing Center of Lomonosov Moscow State University [16].

4. Results and Discussion

Table 1 contains numerical results for the elastic constants of the crystal with parameters $R = 1$, $\sigma_0 = 2$ and $a = 3$.

| Constant | $C$       | $\Delta C_{\text{LMS}}$ | $C$ from [14] |
|----------|-----------|------------------------|---------------|
|          |           | (0.95)                 |               |
| $C_1$    | -1.532724906 | $2.0 \times 10^{-8}$  | 1.53272540    |
| $C_{11}$ | 6.257451   | $2.0 \times 10^{-6}$  | 6.257492      |
| $C_{12}$ | 1.723446   | $2.0 \times 10^{-6}$  | 1.723484      |
| $C_{111}$| -43.4522   | 0.0012                 | –             |
| $C_{112}$| -2.9900    | 0.0009                 | –             |
| $C_{222}$| -36.5130   | 0.0012                 | –             |

Elastic constants of the first and second orders are very close to the same constants obtained earlier in [14] by a different method. The least mean square errors are small although increase with the order of the constants. The third-order elastic constants are all negative making the stress-strain curves convex up. The $C_{222}$ is not equal to the $C_{111}$ in contrast to the second-order case where always $C_{22} = C_{11}$ in the hexagonal lattice. That means that elastic properties of the crystal are not isotropic provided the third-order elastic constants are taken into account.

The third-order elastic constants for the whole range of the lattice parameter $a$ are shown in the figure 2. The absolute value of the constants falls monotonically with the growth of $a$. The curves do not cross each other so that the elastic behavior of the crystals is qualitatively the same for any density.
5. Conclusion
The third-order elastic constants of the model crystals were calculated for the first time. The proposed numerical method proves to be good for calculation of elastic constants of the two-dimensional colloidal crystals up to the third order and possibly higher.

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