Elastic properties of charge-stabilized colloidal crystals with static body-centered cubic lattice

A A Batanova and P E Dyshlovenko

Department of Applied Mathematics and Informatics, Ulyanovsk State Technical University, 32 Severny Venets Street, Ulyanovsk 432027, Russia

E-mail: p.dyshlovenko@mail.ru

Abstract. The model of charge-stabilized colloidal crystals with monatomic body-centered cubic crystal lattice is proposed to determine the first and second order elastic constants of these crystals. The crystals are described within the theory based on the Poisson-Boltzmann nonlinear differential equation. Electric behavior of the colloidal particles obeys the constant charge model. Elastic constants of the crystals are derived from the stress-strain relations obtained by means of the computer experiment. Elastic constants were obtained for a broad range of values of the lattice parameter. Stability of the crystals and the presence of the many-body effective interactions in them are briefly discussed.

1. Introduction

The charge stabilized colloidal crystals are spatially ordered systems of electrically charged submicron particles immersed into a liquid electrolyte. The centers of the particles are located in the nodes of some crystal lattice. Colloidal crystals are used in making photonic crystals and self-organizing structures [1]. These systems are interesting as model systems in the study of ordinary molecular crystals as well as disordered colloidal systems. They also can shed some light onto the more complex systems consisting of micelles, viruses or DNA molecules.

Within the model approach of the present work, colloidal crystals are treated as a medium with initial stress governed by the Poisson-Boltzmann (PB) nonlinear differential equation [2]. This approach does not require any prescribed interparticle potentials since the properties of the system are fully described by solution of the PB equation.

An external pressure is needed for the system of like-charged particles to be stable. For that reason, elastic properties of such systems have some specificity compared to conventional media [3]. In particular, the series expansion of the stress with respect to strain includes a constant term corresponding to the stress in the absence of deformation.

In the paper, we describe a numerical procedure and carry out computer calculations to obtain stress-strain relations for the colloidal crystal with a body-centered cubic (bcc) crystal lattice and constant surface charge density on the particles (cc-model). Elastic constants of the first and second order are then derived from these relations. Knowing the elastic constants we draw a conclusion about mechanical stability of the crystal. We also detect and estimate the many-body effective interaction in the system.
2. Description of the Model

The particles in the colloidal crystal are located in the nodes of the bcc crystal lattice with the lattice parameter \( a \). The particles are charged with constant surface charge density \( \sigma_0 \). The whole array of the particles is embedded into the binary symmetrical univalent electrolyte (1:1 electrolyte).

Electric potential in the crystal obeys the PB equation for the case of the 1:1 electrolyte:

\[
\nabla^2 \varphi = \frac{2q_e n_0}{\varepsilon_0 \varepsilon} \sinh \left( \frac{q_e \varphi}{kT} \right),
\]

where \( n_0 \) is a bulk concentration of any of the two species of the electrolyte, \( q_e \) is the elementary charge, \( \varepsilon \) is a relative dielectric permittivity of the electrolyte, \( \varepsilon_0 \) is the electric constant, \( k \) is the Boltzmann’s constant, and \( T \) is an absolute temperature. To convert equation (1) into the dimensionless form, appropriate for numerical solutions, Debye length \( \kappa^{-1} = \left( \frac{2\varepsilon_0 q_e^2}{\varepsilon_0 \varepsilon kT} \right)^{1/2} \) is used to normalize the distances and \( kT/q_e \) to normalize the electric potential. Only dimensionless quantities are used hereafter in the paper. Then, equation (1) takes the following dimensionless form:

\[
\nabla^2 \varphi = \sinh \varphi.
\]

The PB equation is solved within only a single unit cell due to the spatial periodicity of the crystal. The Wigner–Seitz cell of a bcc crystal lattice is used as a domain for the crystal in equilibrium. In the case of the nonzero strain, the domain is a deformed initial Wigner-Seitz cell. The dielectric permittivity of the electrolyte is assumed to be much greater than the dielectric permittivity of the particle’s material that is pertinent to the aqua solutions. Then, the interior of the particle is excluded from the domain due to the approximation of the infinite dielectric permittivity of the electrolyte. This leads to the following (dimensionless) boundary condition on the surface of the particle:

\[
-\nabla \varphi \cdot \mathbf{n} = \sigma_0,
\]

where \( \mathbf{n} \) is an external unit normal vector of the particle.

A set of faces of the domain is resolved into seven pairs of oppositely located faces. The periodic boundary conditions for the electric potential and its gradient are

\[
\varphi(\mathbf{r}) = \varphi(\mathbf{r} + \mathbf{r}^{(m)}), \quad m = 1, \ldots, 7,
\]

\[
\nabla \varphi(\mathbf{r}) \cdot \mathbf{n}^{(m)} = -\nabla \varphi(\mathbf{r} + \mathbf{r}^{(m)}) \cdot \mathbf{n}^{(m)}, \quad m = 1, \ldots, 7.
\]

Here \( m \) refers to a pair of opposite faces, \( \mathbf{n}^{(m)} \) and \( \mathbf{n}^{(m)} \) are external unit normals to these faces for the \( m \)-th pair, and \( \mathbf{r}^{(m)} \) is a vector of primitive translations separating the faces. In the equilibrium, \( \mathbf{r}^{(1)} = (1, 0, 0) a \), \( \mathbf{r}^{(2)} = (0, 1, 0) a \), \( \mathbf{r}^{(3)} = (0, 0, 1) a \), \( \mathbf{r}^{(4)} = \sqrt{3}/2(1, 1, 1) a \), \( \mathbf{r}^{(5)} = \sqrt{3}/2(1, 1, -1) a \), \( \mathbf{r}^{(6)} = \sqrt{3}/2(1, -1, 1) a \), \( \mathbf{r}^{(7)} = \sqrt{3}/2(1, -1, -1) a \) in the Cartesian coordinate system. Under strain, vectors \( \mathbf{r}^{(m)} \), \( m = 1, \ldots, 7 \), are transformed accordingly.

Equation (2) and boundary conditions (3) and (4) constitute the boundary value problem for the PB equation on the unit cell. Solution of this problem fully describes the properties of the colloidal crystal within the adopted model in any particular spatial configuration, both equilibrium and deformed.

3. Numerical Experiment

The stress-strain relations for the crystals with initial stress are written as follows [3]:

\[
T_{ij} = B_{ij} \delta_{ij} + B_{ijkl} \varepsilon_{kl} + \ldots,
\]

where \( T_{ij} \) is the Cauchy stress tensor, \( \varepsilon_{ij} \) is the infinitesimal strain tensor, \( B_{ij} \) and \( B_{ijkl} \) are tensors of elastic constants of the first and second order respectively, \( \delta_{ij} \) is the Kronecker’s delta-symbol and dots designate the quadratic and higher order terms omitted. The rule of summation over repeating subscripts is implied.
Due to the high symmetry, the bcc crystal has only one independent nonzero elastic constant of the first order, $B_{11}$, and three elastic constants of the second order, $B_{1111}$, $B_{1122}$ and $B_{1212}$. They can be found in two experiments in which the infinitesimal strain tensors have the forms

$$
\begin{pmatrix}
\varepsilon & 0 & 0 \\
0 & \varepsilon & 0 \\
0 & 0 & \varepsilon \\
\end{pmatrix}
$$

and

$$
\begin{pmatrix}
0 & \varepsilon & 0 \\
\varepsilon & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
$$

respectively. Here $\varepsilon$ is a strain parameter that varies during the experiment. The first experiment provides two stress-strain relations

$$
T_{11} = B_{11} + B_{1111}\varepsilon + \ldots,
$$

(7a)

while the second experiment gives

$$
T_{12} = 2B_{1212}\varepsilon + \ldots.
$$

(7c)

Components of the Cauchy stress tensor $T_{ik}$ for charge stabilized colloids are calculated via the fundamental stress tensor $\Pi_{ij}$ associated with the Poisson-Boltzmann equation [4]:

$$
T_{ik} = \frac{1}{V_c} \sum_{k=1}^{7} (m) \int \Pi_{ij} da_j,
$$

(8)

where $r_{ik}^{(m)}$ are components of vectors $r^{(m)}$ described above, $V_c$ is a volume of a unit cell of the crystal and integration is carried out over the surface of the face $S^{(m)}$ indicated by the vector $r^{(m)}$, $m = 1, \ldots, 7$, in each pair of opposite faces of the cell. Stress tensor $\Pi_{ij}$ in (8) is

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

(9)

where $I$ is a unit tensor.

Elastic constants of the crystals with parameters $R = 1$ and $\sigma_0 = 2$ were calculated for the lattice parameter $a$ in range 2.4 to 6.0 in step of 0.1. The unit cell of the crystal was subjected to the two series of deformation described above and corresponding stress-strain relations (7) were obtained. Strain parameter $\varepsilon$ in (6) varied from $-0.01$ to $+0.01$ with step 0.001. An appropriate boundary value problem for PB equation was solved numerically for every given $\varepsilon$. The boundary value problems were solved numerically by the finite element method with gradient irregular meshes of tetrahedral elements. Calculations were partly supported by the Supercomputing Center of Lomonosov Moscow State University [5].

The experimental stress-strain curves were then fitted using standard least square method. The best fitting was obtained with cubic polynomials. Coefficients of these polynomials give needed elastic constants $B_{11}$ and $B_{1111}$, $B_{1122}$, $B_{1212}$.

4. Results and Discussion

Results for the first and second-order elastic constants $B_{11}$ are shown in figure 1. The first order elastic constant $B_{11}$ is just the negative equilibrium pressure $p$, $B_{11} = -p$. The pressure is shown in figure 1a. It decreases monotonically while the lattice parameter increases. The second-order elastic constants are shown in figure 1b. It is worth to notice that elastic constants $B_{1111}$ and $B_{1122}$ are almost equal to each other. The behavior of the second-order elastic constants is also monotonic. Starting from the larger lattice parameter $a$, the curves rise almost exponentially initially while the lattice parameter decreases. Then the rate of growth gets even larger for smaller lattice parameter, being the largest for the $B_{1212}$ elastic constant. Positivity of all the second order elastic constants means that the colloidal crystal with bcc lattice and cc model of the particles is stable relative to the uniform stretch and shear strains within the present model.
Figure 1. Equilibrium pressure (a) and elastic B-constants of the second order (b).

The coefficients in the series expansion of the second Piola-Kirchhoff stress tensor with respect to the components of the Lagrange strain tensor [6] provide another set of elastic constants. These C-constants are related to the B-constants in the following way: $C_{11} = B_{11}$, $C_{111} = B_{1111} - C_{11}$, $C_{112} = B_{1122} + C_{11}$, $C_{1212} = B_{1212} - C_{11}$[3]. The results for the second-order elastic constants $C_{1111}$, $C_{1122}$, $C_{1212}$ are shown in figure 2.

Figure 2. Elastic C-constants of the second order.

Within the one-component model [2], the complex interaction in the colloidal system is reduced to the effective interaction between the particles only. If the effective interaction is pair central, the Cauchy relation $C_{1122} = C_{1212}$ must hold in a static crystal lattice. In our case, the ratio $C_{1122}/C_{1212}$ as function of the lattice parameter $a$ is shown in figure 3. Some interesting oscillations of the ratio are observed for small lattice parameters. The $C_{1122}/C_{1212}$ ratio definitely deviates from the unity for all values of the lattice parameter and varies in the narrow range 0.55 to 0.7. It is worth to notice that the ratio $C_{1122}/C_{1212}$ remains much less than the unity even for big lattice parameters where the pure pair interaction could be expected. This means that the effective interaction between colloids in the crystal is not purely pairwise, and three- and many-body effective interactions can play a role in the system.
Figure 3. Breakdown of the Cauchy relation: the ratio \( C_{1122}/C_{1212} \) strongly deviates from unity.

5. **Conclusion**

The model of charge stabilized colloidal crystals with monatomic body-centered cubic crystal lattice and constant surface charge density on the particles is proposed. The properties of the crystals are derived from the numerical solution to the Poisson-Boltzmann nonlinear differential equation. Numerical procedure for obtaining elastic constants from the stress-strain relations is proposed and applied to the crystals with different values of the lattice parameter. The crystal turns out to be stable relative to small uniform strains in the whole range of the crystal densities studied. The breakdown of the Cauchy relation means than many-body effective potential of some kind should be added to pair potential for proper simulation of the colloidal crystals within the one-component model. This can be of importance for disordered systems as well.

**References**

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