Modeling of elastic properties of charge stabilized colloidal crystals with body-centered cubic lattice

A.A. Batanova[a], P.E. Dyshlovenko[a]

[a] *Ulyanovsk State Technical University, 432027, 32, Severny Venets street, Ulyanovsk, Russia*

Abstract

Elastic properties of charge stabilized colloidal crystals of charged spherical particles with monatomic body-centered cubic crystal lattice are studied numerically. The model of the crystals is based on the nonlinear differential Poisson-Boltzmann equation. Elastic constants of the crystals are derived from the stress-strain dependencies obtained by means of computer experiment. Stability of the crystals and the presence of many-body effective interactions in them are briefly discussed.

Keywords: colloidal crystals; Poisson-Boltzmann equation; elastic constants; many-body interaction;

1. Introduction

The charge stabilized colloidal crystals are spatially ordered systems of electrically charged submicron particles immersed into a liquid electrolyte. Within the model approach of the present work, colloidal crystals are treated as a medium with initial stress governing by the non-linear differential Poisson-Boltzmann (PB) equation [1]. Elastic constants of the first and second order are derived from the stress-strain relations obtained numerically. Owing to the non-zero initial stress, elastic properties of charge stabilized colloidal crystals have some specificity as compared with conventional crystals [2].

2. Description of the Model

Colloidal crystal studied in the present paper is a spatially ordered system of charged colloidal particles embedded into the binary symmetrical univalent electrolyte (1:1 electrolyte). The centers of the particles are located in the nodes of a body-centered cubic (bcc) lattice with the lattice parameter a. The particles are hard spheres of radius R. Electric charge of the particles is uniformly distributed over the surface with constant charge density σ. Crystal with a bcc lattice has intermediate coordination number among the cubic lattices. Elastic properties and stability of such a colloidal crystal were not studied systematically earlier.

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

$$\nabla^2\varphi = \frac{q_e n_0}{\varepsilon_0 \varepsilon}\sinh\left(\frac{q_e\varphi}{kT}\right), \tag{1}$$

where n_0 is a bulk concentration of any of two species of the electrolyte, q_e is the elementary charge, ε is a relative dielectric permittivity of the electrolyte, ε_0 is the electric constant, k is the Boltzmann's constant, and T is an absolute temperature. Using the Debye length $\kappa^{-1} = \left(2n_0 q_e^2/\varepsilon_0\varepsilon kT\right)^{-1/2}$ for measuring distances and unit kT/q_e for electric potential, one can make all the other quantities dimensionless which are only used hereafter in the paper. In particular, equation (1) takes the following dimensionless form:

$$\nabla^2\varphi = \sinh\varphi. \tag{2}$$

The PB equation (2) incorporates the non-linearity of charge distribution with respect to the electric potential, so that the non-linear effects are fully included.

Due to the spatial ordering, the PB equation can be solved within only a single unit cell of the crystal provided the periodic boundary conditions are imposed onto the external boundaries of the cell. The Wigner–Seitz cell of a bcc lattice is used as a domain for the crystal in equilibrium. In the case of non-zero strain, the domain is a deformed initial Wigner-Seitz cell. The interior of the particle is excluded from the domain since the limiting case of large dielectric permittivity of the electrolyte compared to the permittivity of the particles is only studied, which leads to the following (dimensionless) boundary condition on the particle:

$$-\nabla\varphi\cdot\mathbf{n} = \sigma. \tag{3}$$

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

$$\varphi(\mathbf{r}) = \varphi\left(\mathbf{r}+\mathbf{r}^{(m)}\right), \qquad m = 1,\ldots,7, \tag{4a}$$

$$\nabla\varphi(\mathbf{r})\cdot\mathbf{n}^{(m)} = -\nabla\varphi\left(\mathbf{r}+\mathbf{r}^{(m)}\right)\cdot\mathbf{n}'^{(m)}, \qquad m = 1,\ldots,7. \tag{4b}$$

Here m is a number of a pair of opposite faces, $\mathbf{n}^{(m)}$ and $\mathbf{n}'^{(m)}$ are external unit normals of these faces in a 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 basis of 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 configuration. The boundary value problems were solved numerically by the finite element method. Calculations were partly supported by the Supercomputing Center of Lomonosov Moscow State University [3].

3. Numerical Experiment

We use the stress-strain relations in the form that, up to the first order, are written as follows [4]:

$$\Sigma_{ij} = C_{ij}\delta_{ij} + C_{ijkl}\eta_{kl} + \ldots, \tag{5}$$

where Σ_{ij} is the second Piola-Kirchhoff stress tensor, η_{kl} is the Lagrange strain tensor, C_{ij} and C_{ijkl} are tensors of elastic constants of the first and second order respectively, δ_{ij} is a Kronecker's delta-symbol and dots designate quadratic and higher order terms. Elastic constants C_{ijkl} have full Voigt symmetry. Any symbol in the subscripts goes over values 1, 2, 3 that corresponds to x, y and z direction respectively. The common rule of summation over repeating subscripts is implied.

Due to the high symmetry, the bcc crystal has only one independent non-zero elastic constant of the first order, C_{11}, and three elastic constants of the second order, C_{1111}, C_{1122} and C_{1212}. They can be found in two experiments in which the Lagrange strain tensor has the form

$$\begin{pmatrix} \eta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 & \eta & 0 \\ \eta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{6}$$

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

$$\Sigma_{11} = C_{11} + C_{1111}\eta + \ldots, \tag{7a}$$

$$\Sigma_{22} = C_{11} + C_{1122}\eta + \ldots, \tag{7b}$$

while the second experiment gives

$$\Sigma_{12} = 2C_{1212}\eta + \ldots. \tag{7c}$$

The stress tensor Σ_{ij} is related to the Cauchy stress tensor T_{kl} as follows:

$$\Sigma_{ij} = J\gamma_{ik}\gamma_{jl}T_{kl}\ , \tag{8}$$

where γ_{ij} are components of the tensor inverse to the deformation gradient tensor α_{ij}, $J = \det\left[\alpha_{ij}\right]$, and $\alpha_{ij} = \delta_{ij} + u_{ij}$, where u_{ij} is a displacement gradient. Since $\eta_{ij} = 1/2\left(u_{ij} + u_{ji} + u_{ki}u_{kj}\right)$, the only non-zero components of tensor u_{ij} are the following: $u_{11} = -1 + \sqrt{1+2\eta}$ in the first experiment and $u_{11} = u_{22} = -1 + \sqrt{1/2 + \sqrt{1/4 - \eta^2}}$, $u_{12} = u_{21} = \eta/(1+u_{11})$ in the second experiment.

Components of the Cauchy stress tensor T_{ik} are calculated via the fundamental stress tensor Π_{ij} associated with the Poisson-Boltzmann equation [5]:

$$T_{ik} = \frac{1}{V_c}\sum_m r_k^{(m)} \int\limits_{S^{(m)}} \Pi_{ij}\, da_j\ , \tag{9}$$

where $r_k^{(m)}$ are components of vectors $\mathbf{r}^{(m)}$ described above, V_c is a volume of a unit cell of the crystal and integration is carried out over the surfaces of faces $S^{(m)}$ pointed by vector $\mathbf{r}^{(m)}$ in every pair of the opposite faces of the cell. Again, the rule of summation over repeating subscripts is implied. Stress tensor Π_{ij} in (9) is

$$\Pi = \nabla\varphi \otimes \nabla\varphi - (\tfrac{1}{2}\left|\nabla\varphi\right|^2 + \cosh\varphi - 1)I\ , \tag{10}$$

where I is a unit tensor.

Elastic constants of the crystal with parameters $a = 4$, $R = 1$ and $\sigma = 2$ were calculated. The size of the particles is chosen to be compatible with the Debye length which is pertinent to the nanoscale particles in dilute electrolytes. During computer experiments, the unit cell of the crystal was subjected to two series of strain described above and corresponding stress-strain dependencies were obtained. Strain parameter η 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 η.

The experimental stress-strain curves were fitted with polynomials. The best results were obtained with cubic polynomials. Coefficients of these polynomials gave the needed elastic constants C_{11} and C_{1111}, C_{1122}, C_{1212}.

4. Results and Discussion

The results of the numerical experiments are shown in the Table 1. The errors are equal to two standard deviations. The results of the present work are compared with the results obtained by different method described in [6]. In [6], series expansion of the Cauchy stress tensor with respect to the infinitesimal strain parameters was used to obtain an alternative set of elastic constants, B_{11} , B_{1111} , B_{1122} , B_{1212} . Then the *C*-constants can be calculated according to the following relations: $C_{11} = B_{11}$, $C_{1111} = B_{1111} - C_{11}$, $C_{1122} = B_{1122} + C_{11}$, $C_{1212} = B_{1212} - C_{11}$ [2]. The elastic constants obtained by this method for the system studied in the present paper are shown in the third column of the Table 1. Both sets of data are in a very good agreement with each other while the present results have a bit smaller scattering errors. Positivity of all the second order elastic constants means that the colloidal crystal with bcc lattice is stable within the present model.

Table 1. Elastic constants of the bcc crystal

Elastic constant	Present work	According to [6]
C_{11}	-0.3887139 ± 0.0000001	-0.3887138 ± 0.0000002
C_{1111}	1.28586 ± 0.00003	1.2858 ± 0.0001
C_{1122}	0.52833 ± 0.00003	0.52827± 0.00009
C_{1212}	0.59671 ± 0.000013	0.59676 ± 0.00003

To estimate the presence of many-body effective interactions in the crystal, validity of the Cauchy relation $C_{1122} = C_{1212}$ was verified [2]. The ratio C_{1122}/C_{1212} is equal to 0.88539 for the given crystal that is rather far from unity. This means that the effective interaction between colloids in the crystal is not purely pairwise and three- and many-body effective interactions can play some role in the system.

5. Conclusion

Numerical procedure for obtaining elastic constants of charge stabilized colloidal crystals from stress-strain relation is proposed and applied to the crystal with a bcc lattice. The elastic constants demonstrate that the crystal is stable relative to small strains and that the many-body effective interaction should be taken into account for proper description of the elastic properties of the crystal. The preliminary numerical results agree well with the results derived from earlier calculations by alternative method. Calculations for different values of the model's parameters are carrying out at the moment.

References

[1] Belloni, L. Colloidal interactions / L. Belloni // J. Phys.: Condens. Matter.– 2000. – Vol. 12. –P. R549-R587.

[2] Barron, T. H. K. Second-order elastic constants of a solid under stress / T. H. K. Barron, M. L. Klein // Proc. Phys. Soc. – 1965. – Vol. 85. – P. 523-532.

[3] Sadovnichy, V. "Lomonosov": Supercomputing at Moscow State University / V. Sadovnichy, A. Tikhonravov, Vl. Voevodin, V. Opanasenko // In Contemporary High Performance Computing: From Petascale toward Exascale (Chapman & Hall/CRC Computational Science). – Boca Raton, USA: CRC Press, 2013. – P. 283-307.

[4] Holzapfel, G. A. Nonlinear Solid Mechanics: A Continuum Approach for Engineering / G. A. Holzapfel. – Wiley, 2000. – 467 p.

[5] Dyshlovenko, P. E. Osmotic stress tensor in charge stabilized colloidal crystals / P. E. Dyshlovenko // Colloid Journal. – 2010. – Vol. 72(5). – P 627–632.

[6] Batanova, A. A. Modeling of elastic properties of a colloidal crystal with body-centered cubic lattice / A. A. Batanova, P. E. Dyshlovenko // Vuzovskaya nauka v sovremennykh usloviyakh: Proc. of 49th conf. (Jan 26-31, 2015): in 3 volumes. –. Ulyanovsk: UlSTU, 2015. – V. 2. – P. 109-112.