Computer Simulation of Charge Stabilized Colloidal Crystals

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The charge stabilized colloids are systems of electrically charged submicron particles immersed into a liquid electrolyte. There are a lot of examples of such systems in different fields of technology, chemistry and biology. The nature of the particles varies from simplest plastic balls to complex objects like DNA molecules and viruses. In colloidal crystals, the particles form spatially ordered structures so that their centres are located in the vertices of a crystal latice. The charge stabilized colloidal crystals have some technological perspective, especially in photonics. They serve also as model systems of conventional molecular crystals. In addition, studying of colloidal crystals can pour some light onto the disordered systems as well, while presence of spatial ordering simplifies solution of structural problems. The present work is devoted to numerical study of elasticity of charge stabilized colloidal crystals.

Interactions in colloidal systems can be rather sophisticated [1]. Within the model approach of the present work, colloidal crystals are treated as a special medium with initial stress governing by only electrostatic and entropic interactions. The crystals studied are composed of electrically charged hard spheres or circles immersed into binary symmetrical univalent electrolyte (1:1 electrolyte).

The properties of the crystals are described in the framework of mean-field theory leading to the non-linear differential Poisson-Boltzmann equation [1]. In contrast to the linearized theories, the Poisson-Boltzmann equation incorporates the non-linearity of charge distribution with respect to the electric potential, so that the non-linear effects are fully included. The dimensionless Poisson-Boltzmann equation for 1:1 electrolyte has a very simple form:

$$\nabla^2\varphi = \sinh\varphi\,. \qquad (1)$$

Electric charge on the surfaces of particles obeys either constant potential or constant charge density condition. Within the framework of the model, the properties of a colloidal crystal at any particular configuration are fully described by solution of the corresponding boundary value problem for the Poisson-Boltzmann equation. After the solution is obtained, the energy and stress tensor as well as the forces on the particles and osmotic pressure can be easily calculated. The boundary value problem for any particular spatial configuration of colloids was solved numerically. Numerical solution was carried out by finite element method using free tetrahedral meshes of the second order Lagrange elements. Typical discretization contained several millions degrees of freedom. Calculations were partly supported by the Supercomputing Center of Lomonosov Moscow State University [2].

Elastic properties of charge stabilized colloidal crystals in the present work are studied within the approximation of static lattice. Numerical procedures for determination of both the force and elastic constants are described. The force constant determination is based on the perturbation of the ideal lattice by shifting a single particle from its equilibrium position. Elastic constants are directly obtained from the stress-strain dependencies. As it was mentioned above, the charge stabilized colloidal crystals are the systems with initial stress, so that, in contrast to the conventional crystals, the first order elastic constants are not equal to zero.

The force constants and elastic constants of the first and second order were calculated for a wide range of the lattice parameter for different monatomic crystal systems including square and hexagonal lattices in two dimensions and simple cubic, f.c.c. and b.c.c. lattices in three dimensions. The monolayer crystals of spherical particles near charged planes were also considered. Elastic constants obtained from the stress-strain dependencies and calculated from the force constants are in a good agreement with each other. Stability of the crystals relative different types of deformation is discussed.

Pronounced deviation from the Cauchy relations for the elastic constants was observed for all the crystals under study that gives evidence of essential role of the many-body effective interactions in such systems. Some problems of pair and three-body effective interactions in charge stabilized colloids are discussed.

1. Belloni L. *J. Phys.: Condens. Matter*. **12** R549-R587 (2000).
2. Sadovnichy V., Tikhonravov A., Voevodin Vl., Opanasenko V. "Lomonosov": Supercomputing at Moscow State University. In Contemporary High Performance Computing: From Petascale toward Exascale (Chapman & Hall/CRC Computational Science), pp.283-307, Boca Raton, USA, CRC Press, 2013.