Modelling of charge stabilized colloidal crystals

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Elasticity of charge stabilized colloidal crystals is studied numerically within the approximation of static lattice. Description of the colloidal systems is based on the non-linear differential Poisson-Boltzmann equation. Corresponding boundary value problems are solved numerically by finite element method. The force constants and elastic constants of different orders are obtained for different crystal systems both in two and three dimensions. The effective pair and many-body interactions are also studied and discussed.

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 simple plastic balls to complex objects like micelles and DNA molecules. In colloidal crystals, the particles are spatially ordered and located in the vertices of a crystal lattice. 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.

While the interactions in colloidal systems can be rather sophisticated, the electrostatic and entropic interactions are only included in the present study. This allows description by the mean-field theory leading to the non-linear differential Poisson-Boltzmann equation. The properties of a colloidal system at any particular configuration are then fully described by solution of the corresponding boundary value problem for the Poisson-Boltzmann equation. The advantage and disadvantage of such approach is discussed in the present work.

The crystals studied are composed of electrically charged hard spheres or circles immersed into binary symmetrical univalent electrolyte. The appropriate boundary value problems were formulated and solved numerically. Numerical solution was carried out by the finite element method using free tetrahedral meshes of the second order Lagrange elements. Typical discretization contained several millions degrees of freedom while typical computer experiment incorporated up to several thousands of spatial configurations. Calculations were partly supported by the Supercomputing Center of Lomonosov Moscow State University [1].

Numerical procedures for determination of both the force constants and the 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 obtained from the stress-strain dependencies.

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. Stability of the crystals relative different types of deformation is discussed.

Some recently obtained results on the non-linear elastic properties of the crystals are presented. In particular, elastic constants up to the fifth order were calculated for the crystal with two-dimensional hexagonal crystal lattice. The results are compared to the graphene data.

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 effective pair potentials were calculated by solution of the appropriate boundary value problems for the Poisson-Boltzmann equation. The two-dimensional three-body effective potential was also calculated and applied to the description of the elasticity of the colloidal crystals. The problems arising in this study are briefly discussed.

1. 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.