



## Effect of void structures in crystalline structure on the shear moduli of charged colloidal crystals



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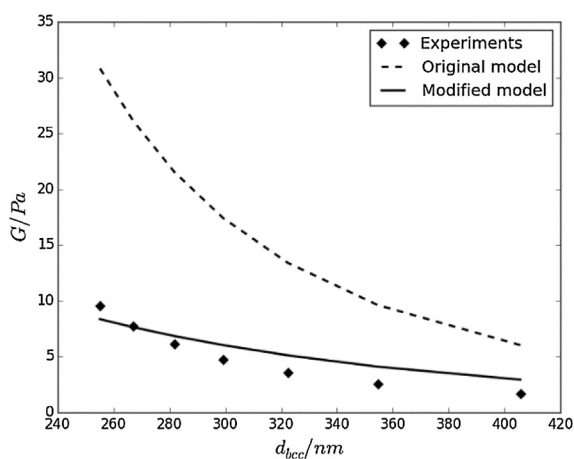
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### HIGHLIGHTS

- Inconsistencies between the theoretical and experimental results for shear moduli are attributed to defects in real crystals.
- Modifications include considering the effect of void structures and using Sogami-Ise potential.
- Modified model is verified by good consistency between theoretical values and experimental results.

### GRAPHICAL ABSTRACT

Shear moduli of colloidal crystals with different nearest inter-particle distances. The results show the consistency between the results of our modified model and the experimental measurements by torsional resonance spectroscopy.



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### ABSTRACT

The existing theoretical model relating shear modulus to inter-particle interaction potential always significantly overestimates the modulus compared with its experimental value for colloidal crystal formed by highly-charged particles. We suppose that such huge disagreements between the theoretical and experimental results are due to that the theoretical model is derived from perfect crystalline structures. To modify the theoretical model, the effect of void defects is introduced to the model and the Sogami-Ise potential model is adopted instead of the commonly used Yukawa potential model. It is shown that with these two modifications the shear modulus model produces results much more consistent with the experimental ones.

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## 1. Introduction

The charged colloidal particles in dispersion can self-assemble into crystalline structures under some appropriate conditions [1–3]. The formed colloidal crystals are analogous to the crystals formed by atoms and molecules and have become valuable model systems of condensed matter particularly because of their easily accessible length and time scales [4,5].

Elastic properties of materials provide an alternative approach [6–9] to understand some physical knowledge comprising the interatomic forces, structures, mechanical features, phase transitions, etc. In this respect the elasticity of the colloidal crystals has been studied in recent years both experimentally and theoretically [10–14]. Experimentally, shear elastic moduli of the colloidal crystals are usually measured through the method of torsional resonance spectroscopy (TRS) in which standing waves are excited when rotary oscillations are imposed on the colloidal crystals [15–17]. In the aspect of theoretical studies, general equations between two-body interatomic potentials in a lattice model and elastic constants were derived for monoatomic solids [18–20]. These equations were later introduced into the systems of colloidal crystals to obtain a shear modulus-potential model that describes the relationship between shear modulus of colloidal crystals and inter-particle potentials [21,22].

Actually, the two-body interaction of charged particles has been formulated with “Yukawa potential” which has a variable – the effective charge of particles. Therefore, by means of the shear modulus-potential model, the shear modulus of colloidal crystals could be estimated when the effective charge of particles in colloidal crystals is known. However, this model has never been used for colloidal crystals to directly determinate the shear modulus. It is reasonable to infer that the value of shear modulus determined by the model using the effective charge would be much larger than the experimentally measured shear modulus  $G$  using TRS. It has been reported that [11], as a matter of fact, the effective shear modulus charge obtained by fitting the measured modulus using this shear modulus-potential model is always much (by about 40%) smaller than the measured effectively transported charge.

Apparently, the theoretical model is valid now only for perfect crystals that contain no imperfections and defects. In practice, however, there are a wide variety of crystallographic defects no matter for atomic crystals or colloidal crystals [23]. Undoubtedly, structural imperfection in crystals would lower their shear moduli. For instance, it was shown [24] that in the bcc-fcc transition process of colloidal crystallization, the shear moduli are much smaller than theoretical expectations and this can be chalked up to crystalline imperfection due to not-well-equilibrated structure during the transition state. Another example demonstrating the structural imperfection is that there exist some void structures in the crystal region of crystals formed by highly-charged colloidal suspensions [12,13,23].

With this regard, the aim of this study is to explore the possibilities of directly using the measured effective charge which is already known to evaluate the shear moduli based on the modified shear modulus-potential model. Previous study [13,25] shows that there is structural imperfection of voids and also Sogami-Ise (SI) interaction potential is more suitable than Yukawa potential for colloidal crystals of highly-charged particles. In this study these two factors were taken into account as modifications to the shear modulus-potential model. The modified model was verified by comparing the theoretical estimation of shear moduli with experimental values measured by TRS. Our results show that the shear moduli evaluated from the modified model are quite consistent with the measured values when the effectively transported charges are used inside the pair-potential model.

## 2. Theory

The shear moduli  $G$  expressed in the original shear modulus-potential model for perfect colloidal crystals with body-centered cubic (b.c.c.) and face-centered cubic (f.c.c.) structures have the following formulas [11,16,22]:

$$G_{bcc}(d_{bcc}) = f_A \frac{3\sqrt{3}}{4d_{bcc}^3} \left( \frac{4}{9} d_{bcc}^2 \frac{\partial^2 V(r)}{\partial r^2} \Big|_{r=d_{bcc}} + \frac{8}{9} d_{bcc} \frac{\partial V(r)}{\partial r} \Big|_{r=d_{bcc}} \right) \quad (1)$$

and

$$G_{fcc}(d_{fcc}) = f_A \frac{\sqrt{2}}{d_{fcc}^3} \left( \frac{1}{2} d_{fcc}^2 \frac{\partial^2 V(r)}{\partial r^2} \Big|_{r=d_{fcc}} + \frac{3}{2} d_{fcc} \frac{\partial V(r)}{\partial r} \Big|_{r=d_{fcc}} \right) \quad (2)$$

where  $d_{bcc}$ ,  $d_{fcc}$  are the nearest inter-particle distance for b.c.c. and f.c.c. structures, respectively,  $V(r)$  is the effective inter-particle interaction pair-potential with  $r$  to be the distance between two particles, and  $f_A$  is a numerical factor that accounts for the different boundary conditions in averaging over randomly oriented crystallites or local environs. Its theoretical limits are  $f_A = 0.4$  for homogeneously distributed strains and  $f_A = 0.6$  for homogeneously distributed stresses, respectively [26,27]. For polycrystalline samples a value of  $f_A = 0.5$  is encountered in most cases [16,28] and will also be used in this work.

The Yukawa potential  $V_{Yukawa}(r)$  which considers Coulomb repulsions only was usually used for  $V(r)$  in this shear modulus-potential model before [11,29,30]. However, experimental observations indicated that there are voids appeared in highly-charged colloidal crystals [12,31,32]. So in addition to the repulsion, inclusion of the counterions-mediated long-range attraction was suggested and then the inter-particle interaction potential was replaced by SI potential [33,34]. The SI potential model, based on the Gibbs free energy of the interaction, not only take into account the large size difference between colloidal particles and small ions, but also relates the variation of macroion charge to the release of counterions. The expressions of Yukawa [11,15,35] and SI pair-potential energy [36,37] are:

$$V_{Yukawa}(r) = \frac{Z_e^2 e^2}{4\pi\epsilon_0\epsilon_r} \left[ \frac{\exp(\kappa a)}{1 + \kappa a} \right]^2 \frac{\exp(-\kappa r)}{r} \quad (3)$$

and

$$V_{SI}(r) = \frac{Z_e^2 e^2}{4\pi\epsilon_0\epsilon_r} \left[ \frac{\sinh(\kappa a)}{\kappa a} \right]^2 \left( \frac{A}{r} - \frac{\kappa}{2} \right) \exp(-\kappa r) \quad (4)$$

where  $Z_e$  is the effective charge number of particles,  $e$  is the elementary charge,  $r$  is the inter-particle distance,  $a$  is the radius of particles, and  $A = 1 + (\kappa a) \coth(\kappa a)$  [25,36]. The parameter  $\kappa$  is the inverse Debye-screening length given by [15,38]:

$$\kappa^2 = \frac{e^2}{\epsilon_0\epsilon_r k_B T} (nZ_e + n_{salt}) \quad (5)$$

where  $n$  is the particle number density of the suspension,  $\epsilon_0\epsilon_r$  the dielectric permittivity of the suspension,  $k_B T$  the thermal energy, and  $n_{salt} = 2000N_{Ac}$  [12,15] the number density of background electrolyte with  $N_A$  being Avogadro constant and  $c$  the molar concentration of foreign salt ( $\text{mol L}^{-1}$ ).

It is obvious that the expressions of shear modulus-potential model shown in Eq. (1) and (2) do not take into account the effect of voids in crystalline structure and they are valid only for perfect crystals. In order to improve this situation there are two factors that can be taken to modify this model: factor 1: taking into account the void defects in crystalline structure; factor 2: inclusion of the attraction in interaction potential model.

For the first factor, we considered that the micro-structure of colloidal crystals is similar to that of cellular solids whose elastic properties have been studied thoroughly for a long time [39–41].

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