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Determination of Elastic Moduli of the r^{-12} Soft Disk Crystal by the Minimum Image Method

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Abstract: Elastic moduli of soft disk crystals close to the melting point have been evaluated by Monte Carlo simulations. The inverse-power potential has been used to model the interactions between particles. In calculations of the elastic moduli by the Parrinello-Rahman formalism, the long-range interactions between atoms have been taken into account using the minimum image method. The study shows that for systems consisting of around a hundred particles there are differences between the values of the elastic moduli obtained by the calculations using the minimum image method and those coming from the traditional approach. It has been found that the elastic moduli obtained by the simulations using the minimum image method even for as small as a hundred-particle systems are very close to these values at the thermodynamic limit $N \to \infty$.

Key words: elastic moduli, inverse-power potential, soft disk crystal, Monte Carlo simulation, minimum image method

I. Introduction

Elastic properties belong to the fundamental physical properties of materials. Determination of elastic properties by computer simulations is an important element that helps in understanding phenomena observed in complex real systems. In simulations, various inter-particle interactions (short and long-range) are used to study the physical properties of the system. One of the fundamental inter-particle potentials in computer simulations is the Lennard-Jones (LJ) potential [1]. Its significant role comes not only from its simplicity but, most of all, from the fact that this model potential allows one to describe the physical properties of noble gases and various properties of simple liquids [1, 2]. The LJ potential is also used as a reference potential to test new theories and computational methods [2]. Application of the minimum image method (MIM) [3, 4] for determining the elastic properties of the LJ system showed that the contribution of long-range interactions cannot be neglected [5]. The LJ potential consists of two parts: attractive ($\sim r^{-6}$) and repulsive ($\sim r^{-12}$). This raises the question of whether the contribution of the repulsive part to long-range interactions influences essentially elastic properties. To answer the posed question we evaluate the elastic properties of the simplest model system, namely a classical two-dimensional system of particles interacting via the inverse-power potential

$$\phi_{ij} = \epsilon \left(\frac{\sigma}{r_{ij}} \right)^{-12}, \tag{1}$$

where r_{ij} is the distance between the interacting particles, σ is the particles' diameter, and ϵ sets the energy scale.

The aim of this work is twofold. Firstly, we determine the elastic moduli of soft disks interacting through the inverse-power potential (1) close to the melting point at thermodynamic limit $N \to \infty$. Secondly, we investigate the influence of long-range interaction on values of calculated elastic moduli using the method of the minimum image that better reproduces the symmetry of the studied solid than the mean-density approximation [5].

II. Method and Computational Details

Simulations of the hexagonal structure of soft disks were performed in periodic boundary conditions. Atoms located in sites of a triangular lattice occupying a rectangular simulation box interact through the inverse-power potential (1). To calculate the elastic properties of soft disk systems, simulations were performed in the NpT ensemble using the Parrinello-Rahman method based on the idea of averaging strain fluctuations [6, 7].

The Gibbs free energy of a two-dimensional hexagonal crystal under an isotropic pressure is [8]

$$G = G(0) + \frac{B}{2} V_p (\varepsilon_{xx} + \varepsilon_{yy})^2 + \frac{\mu}{2} V_p (4\varepsilon_{xy}^2 + (\varepsilon_{xx} - \varepsilon_{yy})^2), \quad (2)$$

where $G(0)$ is the free enthalpy of the system without deformation at pressure p and the reference (equilibrium) volume V_p, B is the bulk modulus, μ is the shear modulus, and ε_{ij} are the components of the strain tensor. More details of the method can be found in Ref. [9].

Alternatively, the elastic properties of the system can be described using Poisson's ratio and Young's modulus instead of elastic moduli. The Poisson's ratio of a two-dimensional isotropic system is

$$\nu = \frac{B - \mu}{B + \mu}, \quad (3)$$

and the Young's modulus reads

$$E = \frac{4B\mu}{B + \mu}. \quad (4)$$

As shown in [5], long-range interactions cannot be neglected when calculating elastic properties and should be appropriately taken into account. In this work, when determining the elastic properties of the system, long-range interactions were considered in two different ways. In the first case, the classical mean-density approximation was used, and in the second, the minimum image method was used.

An accounting of the long-range interactions in computer simulations is computationally quite "expensive". In traditional calculations, the mean-density approximation is used, and the contribution of long-range interactions to the potential energy for the particle i is taken into account by the energy correction ($u_{\rm LRC}$) as follows

$$u_i = \sum_j \phi_{ij} + u_{\rm LRC}, \quad (5)$$

where the sum takes the contribution of the particles in the simulation box for which $r_{ij} < R_{\rm cut}$ where $R_{\rm cut}$ is the cut-off radius (Fig. 1). The second term is the correction of long-range interactions by the mean-density approximation

$$u^*_{\rm LRC} = \frac{\pi\rho^*}{10} \left(\frac{\sigma}{R_{\rm cut}} \right)^{10}, \quad (6)$$

where $u^* = u/\epsilon$ is dimensionless energy, $\rho^* = (N/V)\sigma^2$ is number density, V is volume of the system, and N is the number of particles in the system.

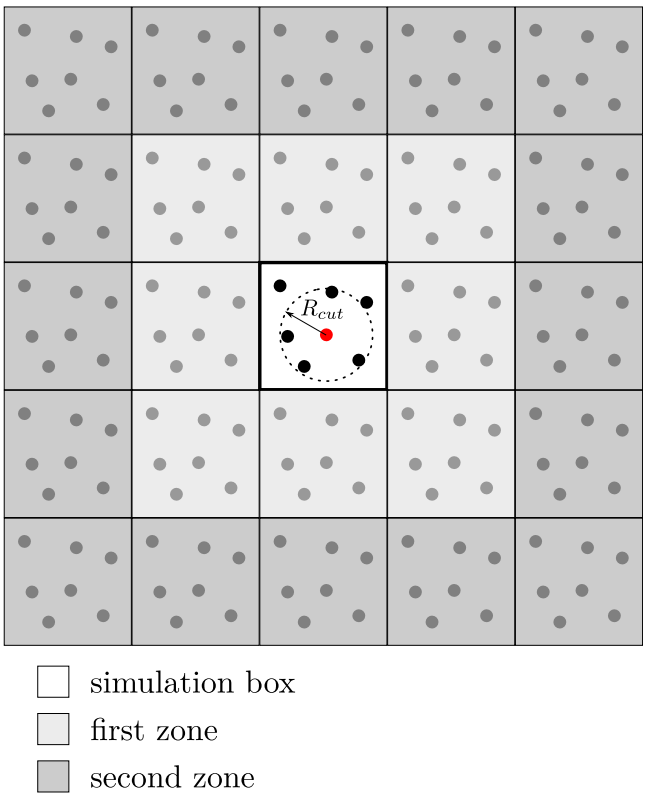

Fig. 1. Simulation box and its images in first and second zones. In the middle is the simulation box with particles denoted as black disks. The first zone is denoted in light grey color. The second zone is shown in dark grey color. The images of particles from the simulation box are shown as grey disks. In the first zone are the nearest images of particles from the simulation box. In the second zone are the next images of particles. $R_{\rm cut}$ is the cutoff radius

In the minimum image method, the calculations of potential energy are performed for the $i^{\rm th}$ particle of coordinates (x_i, y_i) and for the 8 images of the particle with coordinates $(x_i + kL_x, y_i + lL_y)$ where $k, l = -1, 0, 1$ and L_x, L_y are the sides of the simulation box in x and y-directions, respectively. This corresponds to the use of particle images from the first zone (Fig. 1). For the second zone, the calculations of potential energy are performed for the $i^{\rm th}$ particle of

coordinates (x_i, y_i) and for the 24 images of the particle with coordinates (x_i+kL_x, y_i+lL_y) where $k, l = -2, -1, 0, 1, 2$ (Fig. 1). Therefore, the contribution of the nonuniform spatial arrangement of particles (comes from the crystal symmetry) and long-range interactions to the energy due to considering the particle images are taken into account. So, the potential energy of the particle i is [5]

$$u_i = \sum_j \phi_{ij}^{\mathrm{BOX}} + \sum_k \phi_{ik}^{\mathrm{MIM}} + u_{\mathrm{LRC}}, \qquad (7)$$

where the first sum represents the contribution of particles of the simulation box, the second sum describes the contribution of the image particles from outside the simulation box, and the third term is the energy correction of long-range interactions by the mean-density approximation. In the present study, the cut-off radius of the inverse-power potential in Eq. (6) was taken from the condition so that the area of a circle (with radius r_{cut}) equals the area of rectangular (L_xL_y) which was considered in the MIM.

Simulations were performed in dimensionless units: $T^* = k_{\mathrm{B}}T/\epsilon$ is temperature (where k_{B} is the Boltzmann constant), $p^* = p\sigma^2/\epsilon$ is pressure, $B^* = B\sigma^2/\epsilon$ is the bulk modulus, $\mu^* = \mu\sigma^2/\epsilon$ is the shear modulus and the Young's modulus is given by $E^* = E\sigma^2/\epsilon$.

To evaluate the elastic moduli close to the melting point, the Monte Carlo (MC) simulations in the NpT ensembles at $T^* = 1$ and $p^* = 17.45$ were performed for both the classical MC scheme and MC with MIM. Various sizes of the systems to determine the bulk modulus and shear modulus at thermodynamic limit $N \to \infty$ were used in both cases.

The classical Monte Carlo scheme [12] was used with two cutoff radii. In the first case, the samples of $N = 56$, 120, 224, 288, 504, 780, 1024, and 2016 particles were simulated with $r_{\mathrm{cut}} = 2.5\sigma$. In the second case, all particles in the simulation box were taken into account, and for the samples $N = 56$, 120, 224, 288, 504, 780, and 1024 particles $r_{\mathrm{cut}} = (\sqrt[2]{L_xL_y/\pi})\sigma$ were used. Further in the text, this case is denoted as "Box".

Two kinds of MC simulations with MIM were performed. The first kind of simulation concerned the case where the image particles from the first zone were used. The systems consisting of 56, 120, 224, 288, and 504 particles were simulated taking into account 448, 960, 1792, 2304, and 4032 particle images. The second kind of simulation concerned the case where the image particles from the first and the second zones were used. The systems consisting of 56, 120, 224, 288, and 504 particles were simulated by considering 1344, 2880, 5376, 6912, and 12 096 particle images.

In all simulations, two kinds of trial motions were used. The first kind concerned changes in the particle positions, and its acceptance ratio was close to 30%. The second kind of motion corresponded to changes in the components of the symmetric box matrix and was tried about $\sqrt{N}$ times less frequently than the atom motions, and their acceptance ratio was close to 20%. For both traditional MC and MC with MIM, the typical length of the simulation run was equal to 10^7 cycles (trial steps per particle) for all system sizes after equilibration 5×10^5.

III. Results and Discussion

For calculation of the bulk and shear moduli in the thermodynamic limit, four different approaches were used: (i) a spherical truncation (MC: R_{cut}), (ii) all particles in the simulation box (MC: Box), (iii) the minimum image method for the first zone (MIM MC: Box+1), and (iv) the minimum image method for the first and second zones (MIM MC: Box+2).

In the first approach, the elastic moduli were determined based on the classical MC simulations which was considered only for the particles being within the circle diameter $R_{\mathrm{cut}} = 2.5\sigma$ and using the standard amendments to the energy (5). We performed a series of MC simulations with increasing the size of the system. Using extrapolation $N \to \infty$ for the obtained results, the bulk and shear moduli in the thermodynamic limit have been determined. The results of this approach are shown in Fig. 2 by filled circles and the dotted line. There is a strong dependence of the elastic moduli on the size of the system. The results of the second approach (MC: Box), where all particles in the simulation box were taken into account, look similar to the first case (MC: R_{cut}), and still, essential size dependence was observed.

In the third case (MIM MC: Box+1), the bulk and shear moduli were calculated from MC simulations with the method of the minimum image that takes into account all of the particles in the box of periodicity and its nearest images (the first zone). In Fig. 2, the results are presented by the open square and the dashed line of extrapolation determines the value of elastic moduli in the thermodynamic limit. In the last fourth case (MIM MC: Box+2), additionally to all of the particles in the periodic box and its nearest images (the first zone), the images of particles from the second zone are also taken into account in the energy calculation. The results of those calculations are presented in Fig. 2 with open diamonds and black lines. In both cases of MIM MC (Box+1 and Box+2), a very weak dependence on the size of the system is observed for the bulk modulus. This shows results for small systems of the order of 100 particles differ by only a few percent from the values of elastic moduli in the thermodynamic limit. The obtained results confirm that using the minimum image method leads to a much better estimation of the part of the energy related to the deformation of the simulation box than the amendment to the energy based on the mean density approximation. This is especially visible in small systems.

Based on present calculations we obtain the following values of bulk and shear moduli in the thermodynamic limit $(N \to \infty)$ $B^* = 83.7(4)$ and $\mu^* = 24.4(2)$ close to the melting point at $T^* = 1.0$ and $p^* = 17.45$. Besides, it should be stressed that the present calculations also agree with the literature results from Ref. [10] and Ref. [11] (see Fig. 2).

Knowledge of the elastic moduli allows us to calculate Poisson's ratio and Young's modulus using formulas (3) and (4), respectively. The dependence of Poisson's ratio and Young's modulus on the size of systems is presented in Fig. 3. It is interesting to note the weak dependence on the system size of Poisson's ratio for all types of calculations, both classical and MIM MC. However, Young's modulus is strongly dependent on the size of the system in the

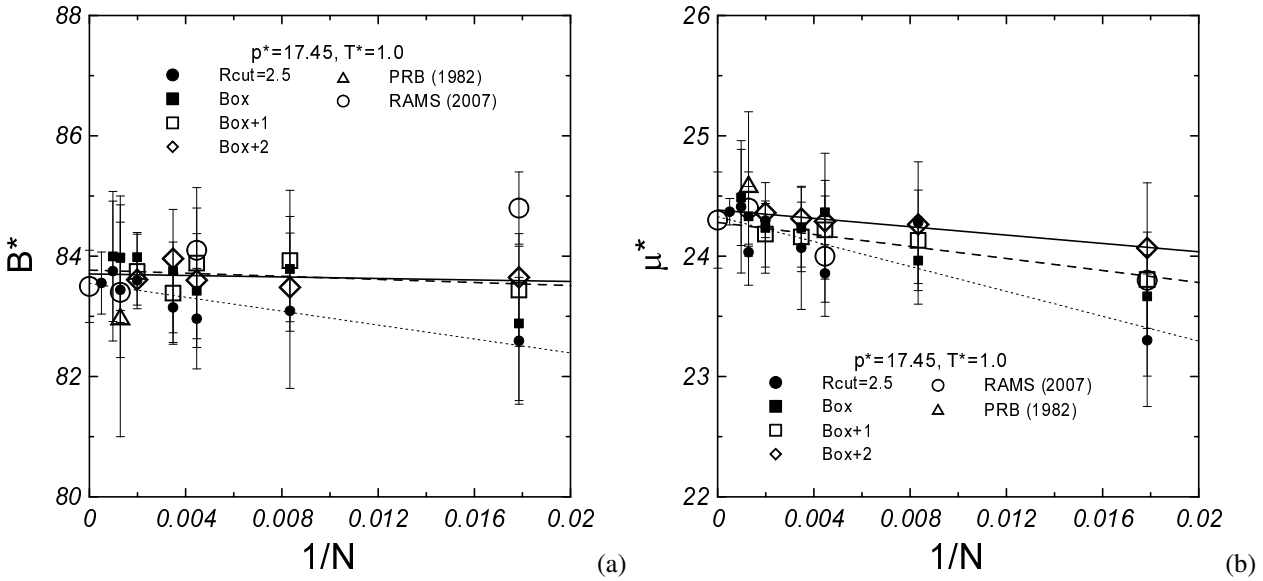

Fig. 2. a) Bulk modulus and b) shear modulus as a function $1/N$ where N is the number of particles in the simulation box. Filled circles represent the results obtained in this work using traditional MC simulations with $R_{\rm cut} = 2.5\sigma$. Filled squares represent the results of simulations where all particles in the simulation box were considered. Open squares correspond to the results of simulations where all particles in the simulation box and their images from the first zone were taken into account. Open diamonds present the results of simulations where all particles in the simulation box and their images from the first and second zones were taken into account. Results of MC simulations are represented in open circles from Ref. [10] and open triangles from Ref. [11]. The dotted line is the linear interpolation to the results of traditional MC simulations with $R_{\rm cut} = 2.5\sigma$ (denoted by filled circles). The dashed line is the linear interpolation to MC results of simulations where all particles in the simulation box and their images from the first zone are considered (denoted by open squares). The black line is the linear interpolation to MC results of simulations where all particles in the simulation box and their images from the first and second zones are considered (denoted by open diamonds)

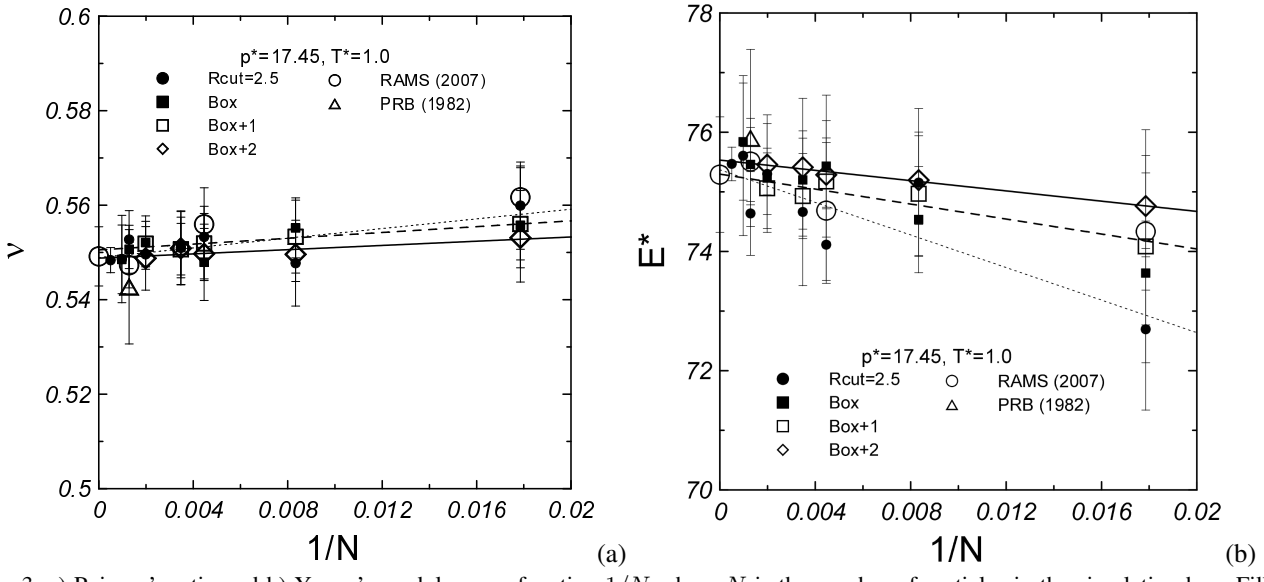

Fig. 3. a) Poisson's ratio and b) Young's modulus as a function $1/N$ where N is the number of particles in the simulation box. Filled circles represent the results obtained in this work using traditional MC simulations with $R_{\rm cut} = 2.5\sigma$. Filled squares represent the results of simulations where all particles in the simulation box were taken into account. Open squares correspond to the results of simulations where all particles in the simulation box and their images from the first zone were considered. Open diamonds present the results of simulations where all particles in the simulation box and their images from the first and second zones were taken into account. Results of MC simulations are represented in open circles from Ref. [10] and open triangles from Ref. [11]. The dotted line is the linear interpolation to the results of traditional MC simulations with $R_{\rm cut} = 2.5\sigma$ (denoted by filled circles). The dashed line is the linear interpolation to MC results of simulations where all particles in the simulation box and their images from the first zone are considered (denoted by open squares). The black line is the linear interpolation to MC results of simulations where all particles in the simulation box and their images from the first and second zones are considered (denoted by open diamonds)

case of traditional calculations and weak in the case of calculations using the minimum image method, similar to the case of bulk and shear moduli. The values of Poisson's ratio and Young's modulus in the thermodynamic limit equal 0.549(7) and 75.5(5), respectively. The above values have been estimated by the extrapolation $N \to \infty$ for the results obtained from MIM MC Box+2 simulations.

IV. Conclusions

The elastic moduli of the soft disk systems in the thermodynamic limit $N \to \infty$ have been calculated in the NpT ensemble using the standard MC simulations and the MC simulation with the minimum image method. The literature data and simulation results obtained in the present work are compared and found in good agreement. The applied method allows one to obtain correct values of the elastic moduli for small systems consisting of around a hundred particles. The Monte Carlo simulations with the minimum image method give a good approximation of the contribution of the part of the energy that takes into account the long-range interactions and better reproduces the symmetry of the studied solid than the traditional approach using the mean-density approximation.

It is worth noting that the contribution of the repulsive part to long-range interactions of such potential as $\sim r^{-12}$ in a two-dimensional system influences essentially elastic properties for small systems only.

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