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Elastic properties of orientationally disordered crystal of mono- and polydisperse hard dumbbells in three dimensions

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Preliminary results concerning influence of polydispersity of ‘atomic’ sizes on elastic properties of the rotator phase of a three-dimensional system of hard dumbbells have been presented. It has been shown that, in contrast to two-dimensional hard discs and three-dimensional hard spheres, for the polydispersity parameter not higher than 5%, there is no significant influence on the elastic constants and Poisson’s ratio of hard dumbbells of the anisotropy parameter 0.15 (i.e., when the discs forming dumbbells are distanced by 15% of the average disc diameter).

Key words: *Monte Carlo simulations; mechanical properties; auxetics; hard body; dumbbells; size polydispersity*

1. Introduction

Elastic properties of materials are important for both fundamental research and practical applications. Recently, a new group of materials exhibiting unusual elastic properties, so called auxetics, have been engineered. These materials undergo lateral expansion (contraction) upon longitudinal tension (compression). Thus, they have a negative Poisson’s ratio which is defined as a negative ratio of transverse strain and the longitudinal strain, when an infinitesimal longitudinal stress is applied. Since such materials may find many important practical applications [1], it is essential to analyze how various microscopic mechanisms may influence elastic properties and Poisson’s ratio itself.

It is worth starting the investigations with well defined model systems and to study how molecular anisotropy and various kinds of disorder can influence the elastic

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*Corresponding author, e-mail: kww@ifmpan.poznan.pl properties of the systems. A crude model of diatomic molecule, the hard dumbbell – a molecule formed by two fused spheres, separated by the distance d – is particularly helpful in this context. This is because it forms an orientationally disordered phase, known as the rotator phase (sometimes referred to as a plastic crystal) which is a thermodynamically stable phase existing between fluid and fully ordered crystalline phase both in two [2] and three [3–6] dimensions. In this phase, while average positions of molecular centres of masses are arranged periodically, molecular orientations are not. Therefore it constitutes a convenient model allowing one to study the role of molecular anisotropy and orientational disorder in macroscopic properties of systems. It is worth mentioning that the rotator phase was experimentally observed in many organic [7, 8] and inorganic compounds [9].

The rotator phase examined in this paper exhibits a regular symmetry. Thus only three elastic constants C_{11}, C_{12}, C_{44} and the pressure p are sufficient for complete description of its elastic properties, including Poissons's ratio. It is worth adding that, from the very definition of Poisson's ratio, it is a direction dependent quantity. For two high-symmetry, longitudinal directions: [100] and [111] (i.e., along the 4- and 3-fold axes respectively), it does not depend on the transverse direction and it can be expressed as [10]

$$\nu_{[100]} = \frac{C_{12} + p}{C_{11} + C_{12}} \tag{1}$$

$$\nu_{[111]} = \frac{1}{2}\frac{C_{11} + 2C_{12} - 2C_{44} + 3p}{C_{11} + 2C_{12} + C_{44}} \tag{2}$$

Poisson's ratios measured along the longitudinal direction [110] and two transverse directions: $[1\bar{1}0]$ and [001], can be respectively expressed as

$$\nu_{[110],[1\bar{1}0]} = \frac{C_{11}^2 - 2C_{12}^2 - \left(5C_{12} - 2C_{44} + 4p\right) + C_{11}\left(C_{12} - 2C_{44} + p\right)}{C_{11}^2 - 2C_{12}^2 + C_{11}\left(C_{12} + 2C_{44} - 3p\right) - \left(5C_{12} + 2C_{44}\right)p} \tag{3}$$

$$\nu_{[110],[001]} = \frac{4\left(C_{44} - p\right)\left(C_{12} + p\right)}{C_{11}^2 - 2C_{12}^2 + C_{11}\left(C_{12} + 2C_{44} - 3p\right) - \left(5C_{12} + 2C_{44}\right)p} \tag{4}$$

The Poisson's ratio averaged over all directions perpendicular to the longitudinal direction [110] is equal to the mean of right hand sides of Eqs. (3) and (4).

2. The system studied

Monodisperse hard dumbbell (i.e., with both 'atoms' having the same diameters σ), can be characterized by the reduced bond length $d^* = d/\sigma$ measuring the molecular anisotropy. Elastic properties of monodisperse, hard dumbbell rotator phase have been investigated for five distinct molecular anisotropies, namely 0.05, 0.10, 0.15, 0.20, and 0.30 [10]. In the current, preliminary report, we restrict our attention to $d^* = 0.15$ and analyze the system in which the 'atomic' diameters forming the dumbbells are no longer equal. Instead, they were generated randomly according to the Gaussian distribution with the average equal to $\sigma \equiv \langle \sigma_i \rangle$ and with the fixed standard deviation

$$\delta = \frac{\sqrt{\left\langle \sigma_i^2 \right\rangle - \left\langle \sigma_i \right\rangle^2}}{\left\langle \sigma_i \right\rangle^2} \tag{5}$$

treated as a polydispersity parameter. Such models can play important roles in understanding properties of real man-made systems of micro-, mezo- and macroparticles [11, 12] which commonly are not perfectly identical.

As was mentioned before, interaction between 'atoms' of the molecules is hard, i.e. infinite when any overlap occurs among the particles and zero otherwise.

3. Results

In both cases, i.e. for mono- and polydisperse hard dumbbells, a variant of constant pressure MC simulations was used in which periodic box can alter its size and shape [13–15]. Runs consisted of 10^7 MC cycles (after equilibration). The acceptance ratio for combined translational-orienational moves was kept at the level of 25%, while the acceptance ratio for volume changes was equal 20%. In the monodisperse case, the dumbbell mass centres were initially arranged in the fcc lattice, whereas their orientations were aligned with z axis. For the polydisperse system, starting from α-N_2 structure appeared to be more convenient. The initial lattice constants were chosen large enough to eliminate overlaps. Since the method applied shows rather small dependence of results on the system size, systems consisting of $N = 108$ molecules were used. Three different values of the polydispersity parameter δ were studied: 0.01, 0.03, and 0.05 for the system of hard dumbbells with the anisotropy $d^* = 0.15$. The values presented below are the averages obtained for three different runs for each anisotropy and each polydispersity.

In Figure 1, one can see how polydispersity affects elastic constants C_{ij} of a hard dumbbell rotator phase. It can be seen there that the polydispersity of 'atomic' sizes has no visible impact on the constants C_{11} and C_{12}. Their values, for different δ, are practically indistinguishable from the results obtained in the case of monodisperse system. For C_{44}, the situation is slightly different. A systematic increase of its value is observed, for increasing value of the polydispersity as the system approaches the transition between the rotator phase and the (high pressure) crystalline phase.

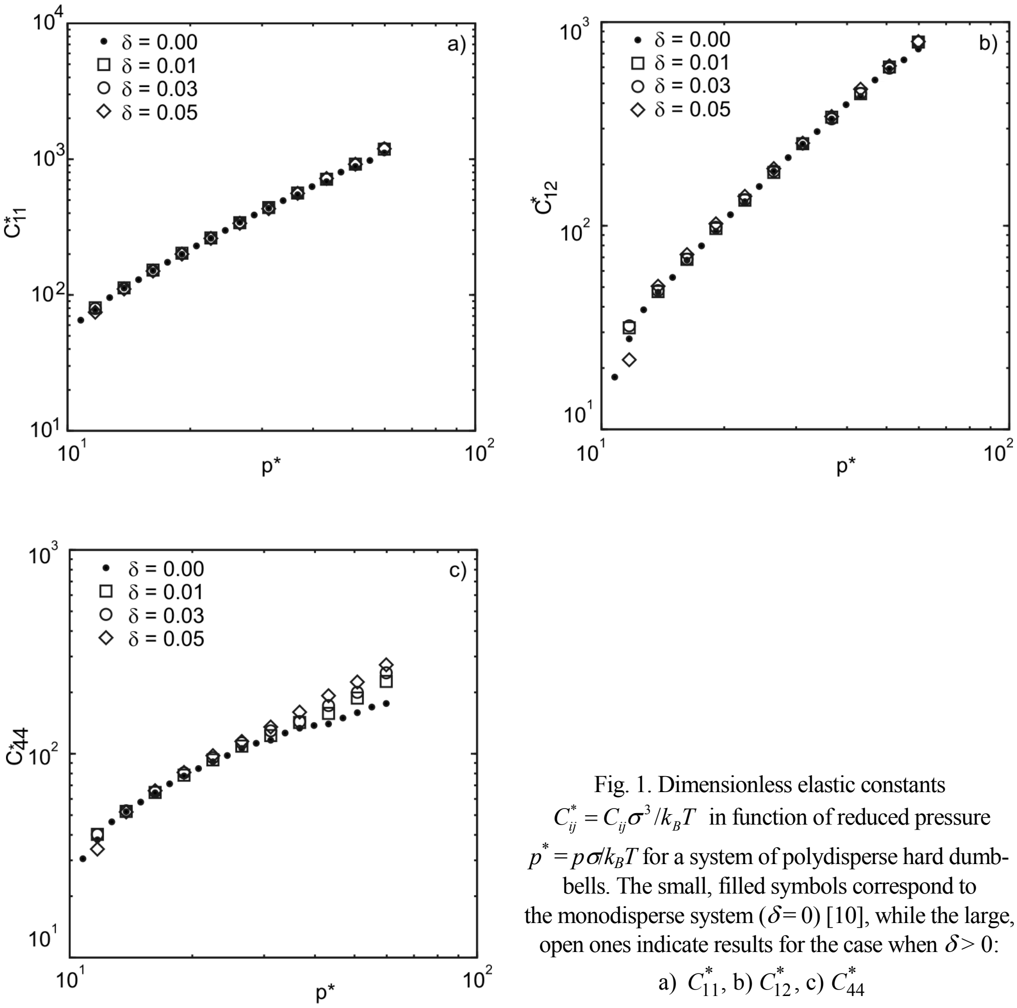

Fig. 1. Dimensionless elastic constants $C^*_{ij} = C_{ij}\sigma^3/k_BT$ in function of reduced pressure $p^* = p\sigma/k_BT$ for a system of polydisperse hard dumbbells. The small, filled symbols correspond to the monodisperse system ($\delta = 0$) [10], while the large, open ones indicate results for the case when $\delta > 0$: a) C^*_{11}, b) C^*_{12}, c) C^*_{44}

The system Poisson's ratio seems to be a more appropriate indicator of changes in system properties introduced by polydispersity [16]. Its behaviour measured in three different longitudinal directions: [100], [111], and [110] (the latter is averaged over corresponding transverse directions) is shown in Fig. 2. One can see that Poisson's ratio reflects the alterations of amount of polydispersity of 'atomic' sizes more accurately than the elastic constants. When the system approaches the melting transition, Poisson's ratios along all measured directions slightly grow with the increasing polydispersity parameter. It is interesting to note that for directions [111] and [110], the values of the Poisson's ratio decrease (not much, however) when the pressure increases, i.e. when the system approaches the crystal–rotator phase transition.

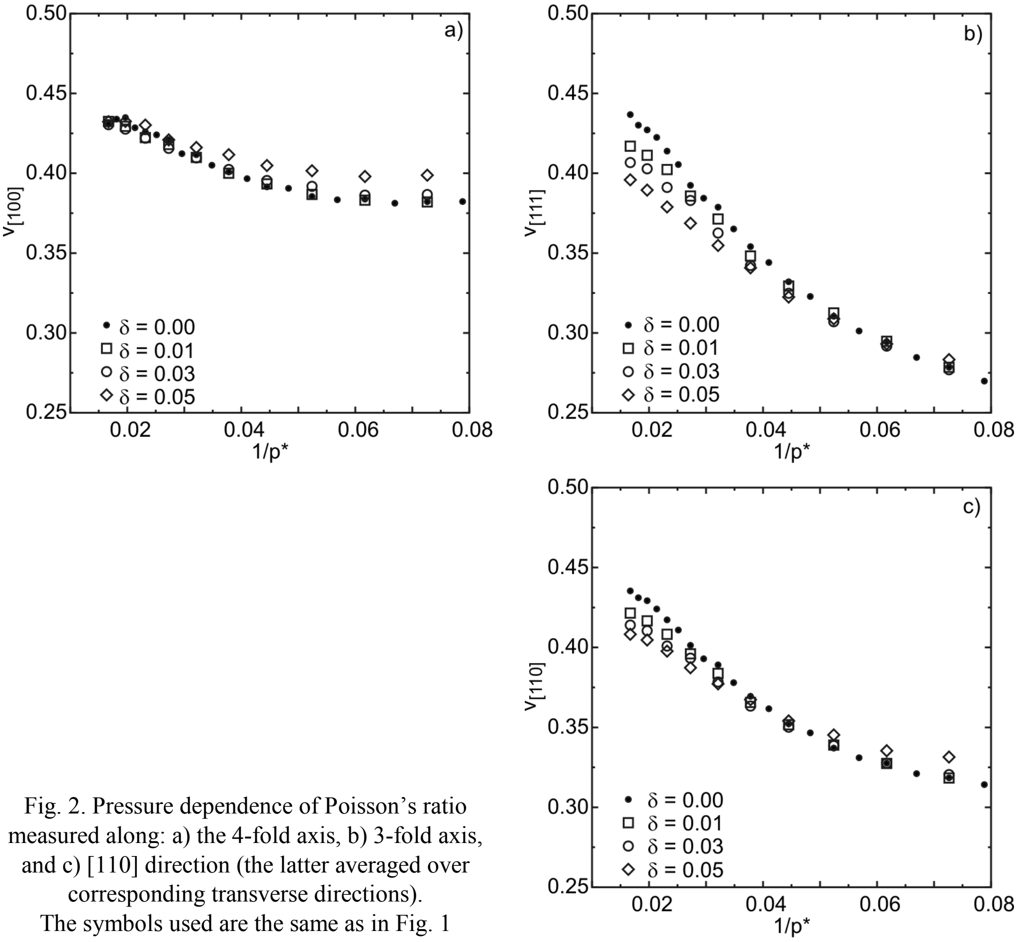

Fig. 2. Pressure dependence of Poisson's ratio measured along: a) the 4-fold axis, b) 3-fold axis, and c) [110] direction (the latter averaged over corresponding transverse directions). The symbols used are the same as in Fig. 1

4. Conclusions

Current preliminary studies, show that polydispersity of 'atomic' sizes (not greater than 5%) only slightly affects the elastic properties of the hard dumbbell rotator phase, for the molecular anisotropy parameter $d^* = 0.15$. Only minor changes in values of elastic constants and measured Poisson's ratios are observed. The obtained result is rather surprising in the context of previous numerical evidence for polydisperse hard discs [17] and hard spheres [18] which indicated strong influence of particle polydispersity on elastic properties of those systems. It seems that elastic properties of the rotator phase are determined mainly by the orientational disorder [10] and the polydispersity of 'atomic' sizes plays rather minor role, at least for polydispersity of atomic sizes not exceeding 5 percent. It is attractive to conjecture that the present conclusion holds true in the whole range of the anisotropy and polydispersity parameters for which the rotator phase of hard dumbbells is stable. Work on this question is in progress.

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