Elastic properties of degenerate f.c.c. crystal of polydisperse soft dimers at zero temperature

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Elastic properties of soft, three-dimensional dimers, interacting through site-site n-inverse-power potential, are determined by computer simulations at zero temperature. The degenerate crystal of dimers exhibiting (Gaussian) size distribution of atomic diameters – i.e. size polydispersity – is studied at the molecular number density \( \frac{1}{\sqrt{2}} \); the distance between centers of atoms forming dimers is considered as a length unit. It is shown that, at the fixed number density of the dimers, increasing polydispersity causes, typically, an increase in pressure, elastic constants and Poisson’s ratio; the latter is positive in most directions. A direction is found, however, in which the size polydispersity causes a substantial decrease in Poisson’s ratio, down to negative values for large \( n \). Thus, the system is partially auxetic for large polydispersity and large \( n \).

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1. Introduction

Elastic properties are those among the characteristics of real materials that are crucial from the point of view of various applications. Recently, increasing interest has been observed in the area of materials with unusual elastic properties—an example are materials with negative Poisson’s ratio [1–7]. When stretched (or compressed) such materials increase (decrease) their size not only in the direction of the stretch (compression) but also in one or more directions transverse to it [7]. Materials exhibiting such counterintuitive behavior are known as anti-rubber [8], dilational materials [9] or auxetics [2]. In this paper, the last name will be used for its brevity.

As for isotropic systems, Poisson’s ratio is direction independent, any isotropic material can be either auxetic or not. For anisotropic systems, which are the subject of the present paper, the situation is more complex. Apart from the alternative that Poisson’s ratio is negative or not in all directions, a third possibility exists: in some directions it is negative and in other—it is not. In the literature related to the field, various names have been proposed to describe different situations [4,10–12]. Here we will adopt the scheme introduced in Ref. [12], in which – as in the isotropic case – the names auxetics and nonauxetics correspond, respectively, to negative or non-negative Poisson’s ratio in all directions. Materials with Poisson’s ratios negative in some directions and nonnegative in the other ones will be referred to as partially auxetic materials or just partial auxetics.

The very existence of auxetics and partial auxetics encourages one to study the influence of various micro-level mechanisms on the elastic properties of condensed matter [13–44]. An important problem in this context is the influence of disorder on Poisson’s ratio. For some two-dimensional (2D) models which are elastically isotropic (at least for small deformations) and for some anisotropic 2D models, it has been found that various kinds of disorder (such as vacancies, interstitials, aperiodicity or polydispersity) introduced in crystalline structures increase Poisson’s ratio [45–50]. Studies of some three-dimensional (3D) molecular models [51] have revealed similar effect caused by vacancies, what might suggest a general conclusion that (at least in simple molecular systems) disorder weakens or eliminates auxeticity.

Recently, however, it has been found that in one of the simplest 3D systems—soft spheres, forming the f.c.c. phase, there exists a direction in which one of the form of disorder (polydispersity) decreases Poisson’s ratio, which reaches negative values down to \(-1\) [52]. This observation might find practical applications, e.g. in production of partial auxetics of latex meso or macroscopic spheres for which size polydispersity is easy to control. Unfortunately, the mentioned lowest Poisson’s ratios have been observed only for the softest spheres with \( n = 6 \), i.e. when the f.c.c. structure may be unstable with respect to the b.c.c. structure [53].

Taking into account the fact that elastic properties of many-body systems strongly depend on the details of the intermolecular interaction potential and, in particular, on the molecular shape, it is interesting to study other 3D systems searching for stable structures...
for which increasing polydispersity can lead to more negative Poisson’s ratios in some directions. As it is meaningful to start with the simplest molecular shapes, the natural candidate for a first 3D molecule to investigate is a polydisperse dimer.

The aim of this study is to determine the influence of disorder introduced to a solid of soft dimers by the size dispersion of their atoms, on the elastic properties of the model. The study concerns the zero temperature, \(T = 0\), and the number density \(N / V = 1/\sqrt{2}\), where \(V\) is the volume and \(N\) is the number of dimers. At this density atoms of dimers can be arranged in a perfect f.c.c. lattice of the lattice constant equal to the distance of atomic centers in the dimer. The dimers form a degenerate crystalline (DC) phase — an analogue of that observed in 2D [54]. The phase is characterized by non-periodic positions and orientations of molecules, whereas the atoms forming molecules are arranged in a perfect f.c.c. lattice (when the atoms are identical) or (for slightly different sizes of atoms) in a lattice close to the f.c.c. one. The DC phase is known to be thermodynamically stable and effectively cubic from the point of view of elastic constants for hard dimers [55] and is expected to preserve those properties for soft dimers with short ranged interactions which are studied in the present paper.

The soft dimer system can be seen as a rough model of some man-made nano-, meso- or macro-particle systems, e.g. systems of latex particles [56,57]. Recently, an increasing interest has been observed in systems of soft particles [58], especially in the context of physics of colloids. This is due to the fact that the latter have a broad range of possible applications. Systems of soft polydisperse particles seem to be more realistic models of colloids than those built of identical particles. Polydispersity is also important for nanoparticle crystals [59–61], where the speed of crystallization and resulting crystal quality is strongly related to the size dispersion of particles.

Studies of elastic properties of models of polydisperse systems can be thought of as a first step on a path to a better understanding of the mechanisms and phenomena that govern the elastic properties of real systems. Such knowledge is not only important from the point of view of fundamental research but also useful from the material engineering point of view — it can help to engineer materials with desired elastic properties.

2. Description of the studied model

The model studied in this work consists of \(N\) diatomic molecules (dimers) in periodic boundary conditions. The dimers are rigid i.e. the distance between centers of the atoms forming each one is constant and equal to \(\sigma\) (which constitutes a unit of length) for each dimer. Initially the atoms form a perfect f.c.c. lattice and the molecules form a degenerate crystalline (DC) phase. The atoms interact via purely repulsive potential of the form:

\[
u_{ij}(d_j, r_j) = u_0 \left( \frac{d_j}{r_j} \right)^n,
\]

where \(d_j = (d + d_j)/2\), \(d\) and \(d_j\) are the diameters of the interacting spheres (atoms), \(r_j\) is the distance between their centers and \(u_0\) is the energy unit. The exponent \(n\) is further referred to as the hardness parameter and its inverse, \(1/n\), as the softness parameter. (These names come from the observation that when \(n \to \infty\) the interaction potential described by Eq. (1) tends towards the hard-body potential which is widely used in computer simulations and condensed matter theory [34].) Atomic interactions are assumed to be short-range, i.e. only the nearest neighbors (shearing a face of their Voronoi polyhedra) interact. Since the molecules are considered as rigid, interactions between atoms forming a molecule are neglected.

2.1. Atomic size polydispersity

In the studied system, atomic diameters were generated randomly according to the Gauss distribution function with a given standard deviation \(\delta\):

\[
\delta = \frac{1}{\sigma} \sqrt{\langle d^2 \rangle - \langle d \rangle^2}.
\]

In the above equation, \(d\) is the atomic diameter and \(\sigma = \langle d \rangle\). Further in this work, \(\delta\) is treated as the measure of disorder in the system and is referred to as the polydispersity parameter. The generated values of atomic diameters were randomly distributed among atoms in the structure. In Fig. 1 examples of the studied structures are presented. It can be seen that even in the presence of atomic size polydispersity atoms form a nearly perfect f.c.c. lattice.

3. Basic formulae

In the following, it will be assumed that the studied system of soft dimers exhibits an effective regular symmetry. For the latter symmetry, when the external pressure \(p\) is zero, elastic properties can be described by just three elastic constants \(C_{xxx}, C_{yyx}\) and \(C_{zzy}\) [62]. However, when \(p \neq 0\), it is more convenient [22,45] to use other elastic constants, \(B_{ijkl}\), obtained by expanding the free enthalpy (Gibbs free energy), \(G\), with respect to the components of the Lagrange strain tensor, \(\varepsilon\):

\[
\Delta G / V_{ref} = \Delta (F + pV) / V_{ref} = \frac{1}{2} \sum_{ijkl} B_{ijkl} \varepsilon_{ij} \varepsilon_{kl}.
\]

![Fig. 1. Example of studied structures with atomic size polydispersity. The structure shown consists of 432 molecules and has the polydispersity parameter \(\delta\) equal to 15. In a) the atoms are drawn in the shades of gray, indicating their size relative to other atoms. The ones drawn in white are the smallest and those drawn in black are the largest. The gray cube indicates the periodic box. In b) connections between atoms in the same structure as in a) are shown.](image)
\( F \) in the above equation is the (Helmholtz) free energy and \( V_{\text{ref}} \) is the volume of the deformation-free (reference) system. The elastic constants \( B_{ijkl} \) are simply related to the constants \( C_{ijkl} \) \[63,64\]:

\[
B_{ijkl} = C_{ijkl} - p(\delta_i\delta_j + \delta_k\delta_l - \delta_i\delta_k - \delta_j\delta_l).
\]

where \( \delta \) is the Kronecker delta, equal to 1 for \( i=j \) and zero otherwise.

In the case of cubic symmetry, considered in this work, only the following elastic constants are of interest (the Voigt notation is used below \[63\]):

\[
B_{11} = C_{11} - p, \quad B_{12} = C_{12} + p, \quad B_{66} = C_{66} - p.
\]

and the free enthalpy expansion \( (3) \) takes the form:

\[
\Delta G / V_{\text{ref}} = \frac{1}{2} B_{11} (\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + B_{12} (\varepsilon_{xy}^2 + \varepsilon_{yx}^2 + \varepsilon_{zx}^2 + \varepsilon_{xz}^2) + 2B_{66} (\varepsilon_{yu}^2 + \varepsilon_{yu}^2 + \varepsilon_{u2}^2 + \varepsilon_{u2}^2).
\]

4. Numerical determination of elastic properties

In order to obtain the elastic constants, a sample was considered which, at equilibrium, is described by three vectors \( a_0, b_0, \) and \( c_0 \) parallel to the unit cell edges of the f.c.c. lattice. The components of those vectors form columns of a reference box matrix \[66,67\] \( H \). Applying a uniform deformation that transforms the sample into a parallelepiped described by the box matrix \( h \) one can write the Lagrange strain tensor in the form \[66,67\]:

\[
\varepsilon = \left( H^{-1} \ Quadrant10 \right) / 2.
\]

where \( h' \) is the transposed matrix \( h \) and \( I \) is the unit matrix. Differentiating the free energy \( F \) with respect to the strain tensor components, one obtains all the elastic constants and pressure. It is worth noting that in the case of zero temperature (\( T=0 \) K), the free energy is just equal to the potential energy of the system.

For cubic systems, instead of constants defined by Eqs. (5)–(7), the below elastic moduli are also often used:

\[
B = \frac{1}{3} (B_{11} + 2B_{12}),
\]

\[
\mu_1 = B_{66},
\]

\[
\mu_2 = \frac{1}{2} (B_{11} - B_{12}).
\]

where \( B \) is the bulk modulus, and the \( \mu \) are the shear moduli. In the following, both the sets of quantities will be used while presenting and discussing the results.

Poisson’s ratio is defined as the negative ratio of transverse to longitudinal strain when only the longitudinal component of the stress tensor is infinitesimally changed. For anisotropic systems it depends, in general, on both the longitudinal and the transverse direction. For cubic symmetry, Poisson’s ratio along two high-symmetry longitudinal directions ([100] and [111]) does not depend on the choice of the transverse direction [10] and can be expressed by the elastic constants, \( B_{0} \), in the form \[65\]:

\[
v_{1[100]} = \frac{B_{12}}{B_{11} + B_{12}} = \frac{1}{2} \frac{3B - 2\mu_1}{3B + \mu_1},
\]

\[
v_{1[111]} = \frac{B_{11} + 2B_{12} - 2B_{66}}{2(B_{11} + 2B_{12} + B_{66})} = \frac{1}{2} \frac{3B - 2\mu_1}{3B + \mu_1}.
\]

In this paper, Poisson’s ratio along the longitudinal direction [110] and two transverse directions [110] and [001] was also computed:

\[
v_{1[110][10]} = \frac{B_{12}^2 + B_{11}B_{12} - 2B_{12}^2 - 2B_{11}B_{66}}{B_{11} + B_{12} - 2B_{12}^2 + 2B_{11}B_{66}} = \frac{3B(3\mu_2 - \mu_1) - 4\mu_1\mu_2}{3B(3\mu_2 + \mu_1) + 4\mu_1\mu_2},
\]

\[
v_{1[110][001]} = \frac{4B_{11}B_{66}}{B_{11} + B_{12} - 2B_{12}^2 + 2B_{11}B_{66}} = \frac{6\mu_1\mu_2 - 4\mu_1\mu_2}{3B(3\mu_2 + \mu_1) + 4\mu_1\mu_2}.
\]
After determining the equilibrium positions and orientations of all the molecules in the reference state for a given $\delta$, the following deformations were applied:

$$h_{\alpha\beta} = (1 + \xi_{\alpha}) H_{\alpha\beta} \delta_{\alpha\beta},$$

for which new equilibrium positions and orientations were determined. In (17) $\alpha, \beta$ indicate directions, and $\xi_{\alpha}$ is a small real number. The relations below define the elastic constants and pressure:

$$\frac{\partial F}{\partial \xi_{\alpha}} \bigg|_{\xi_{\alpha}=0} = -p,$$

$$\frac{\partial^2 F}{\partial \xi_{\alpha}^2} \bigg|_{\xi_{\alpha}=0} = B_{11},$$

$$\frac{\partial^2 F}{\partial \xi_{\alpha} \partial \xi_{\beta}} \bigg|_{\xi_{\alpha}=\xi_{\beta}=0, \alpha \neq \beta} = B_{12} - p.$$
The $B_{66}$ constant was obtained by applying the deformation of the form:

$$
\begin{align*}
    h_{\alpha\alpha} &= H_{\alpha\alpha}, \\
    h_{\alpha\beta} &= H_{\alpha\beta} + \xi_{\alpha\beta} H_{\alpha\alpha},
\end{align*}
$$

for which new equilibrium positions and orientations were determined. In (21) $\xi_{\alpha\beta} = \xi_{\beta\alpha}$ is a small real number. For $H_{xx} = H_{yy} = H_{zz}$ this leads to the following:

$$
\frac{\partial^2 F}{\partial \xi_{\alpha\beta}^2} \bigg|_{\xi_{\alpha\beta} = 0} = 6(2B_{66} + p).
$$

5. Results

In Fig. 2 (a) and (b) values of the pressure and the bulk modulus are shown, respectively. It is clearly visible that increasing the polydispersity and increasing $n$ leads to an increase in those quantities as was earlier observed in other systems [47–50,52].

The observed behavior can be qualitatively understood by noticing that dense packing of identical molecules in the hard-body limit requires less space than dense packing of polydisperse molecules of the same average size [46]. As all the considered systems are studied at the same volume, their densities relative to close packing grow with the increasing polydispersity. An increase in the relative density implies an increase in the pressure and the bulk modulus. Obviously, the latter quantities show the largest increase for the largest $n$, when the interaction potential is the steepest one.

In Fig. 3 the elastic constants $B_{ij}$ are shown. It can be seen that all elastic constants also increase with increasing polydispersity and the increasing value of $n$. The presented behavior of elastic constants is also similar to that observed for other 2D and 3D systems [47–50,52] and can be qualitatively explained by the close packing argument used above.

In Fig. 4 plots of $\mu / B$ ratios are presented. As in the case of earlier studies [47–50,52] for both 2D and 3D, these ratios seem to tend towards 0 for any nonzero polydispersity, in the hard interactions limit ($n \to \infty$).

According to the formulae (12) and (13) the above mentioned asymptotics of $\mu / B$ implies that the system behaves like rubber.
where most negative values of Poisson’s ratio were observed for small and large studied, Poisson’s ratio of the high-symmetry axes. It is worth noticing that in the cubic system phase of 2D dimers [49], is of interest from the point of view of production of partial auxetics. As shown in Fig. 5(d), a solid structure observed in the case of 2D [47]

significant. This new behavior of Poisson’s ratio is opposite to what was discovered in the polydisperse soft sphere system [52], where most negative values of Poisson’s ratio were observed for small n only.

The observed dependence of \( \nu_{\text{110}(110)} \). Surprising in the context of the results obtained for various 2D isotropic systems including the DC phase of 2D dimers [49], is of interest from the point of view of production of partial auxetics. As shown in Fig. 5(d), a solid structure of dimers obtained by ‘gluing’ together pairs of polydisperse soft spheres arranged in the f.c.c. lattice will show Poisson’s ratio as low as \( \nu_{\text{110}(110)} = -0.8 \).

6. Conclusions

The elastic properties of a polydisperse soft dimer system in three dimensions were studied by computer simulations in the static (zero temperature) case. Disorder was introduced to the DC f.c.c. structure in the form of atomic size dispersion with polydispersity parameter \( \delta \). The influence of polydispersity on the elastic properties of the 3D DC dimers system was determined. It was found that the increasing of polydispersity and hardness of the interaction potential caused a significant increase in the elastic constants and pressure.

The simulations showed that Poisson’s ratio of the dimer system measured in [100] and [111] directions increased to its maximum positive value, 1/2, in the presence of any nonzero polydispersity and sufficiently hard interaction potential. An increase in Poisson’s ratio was observed also in other directions. Such behavior had been earlier observed in the case of 2D [47–50] and 3D [52] systems and seems to be a typical result.

However, it is worth stressing that for the longitudinal direction [110] and transverse direction [110] Poisson’s ratio decreases reaching negative values along with increasing the polydispersity value both for large and small n. This unusual phenomenon is of interest from the point of view of manufacturing stable auxetics of cubic symmetry.

The questions whether the effect of auxeticity enhancement by polydispersity is characteristic for the f.c.c. lattice only or if it can be observed for elastic symmetries other than the f.c.c. one, e.g. for packing of spheres in an h.c.p. lattice or stacking fault lattices, will be the subject of a separate paper. Studies of elastic properties of other molecular shapes are in progress.

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