

1 Introduction

The Poisson's ratio describes the change in transverse and longitudinal dimensions of a material with respect to an applied longitudinal stress (stretching or compressing). Typical materials show positive Poisson's ratio. In recent years an intense search for materials with *negative* Poisson's ratio [1], also called *auxetics* [2], has been conducted. Such materials behave in opposite way to that we see every day (see Fig. 1), i.e. they increase (decrease) their dimensions in one or more transverse directions when longitudinally stretched (compressed). This uncommon behavior gives these materials a wide range of possible applications [1, 3–6].

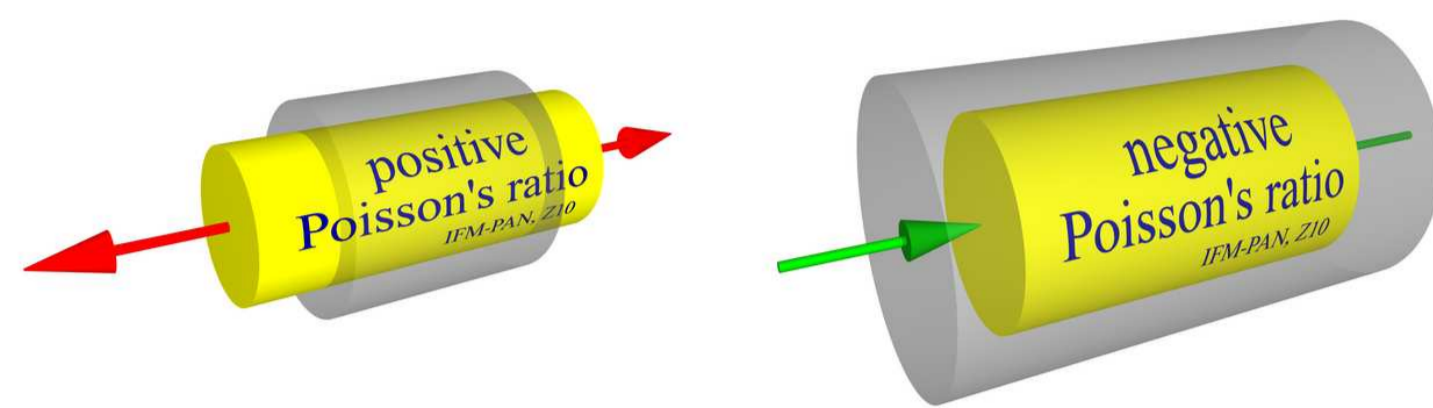


Figure 1. Examples of conventional material with positive Poisson's ratio (to the left, while stretched the sample gets thinner) and the material with negative Poisson's ratio (to the right). Contrary to the conventional material, the auxetic gets thinner when compressed. The gray shape shows the material's initial (undeformed) state.

Better understanding of mechanisms behind auxeticity can be achieved by analyzing simple models. Recently, it has been shown that, at zero temperature, planar three-atomic molecules of 3-fold symmetry axis (further called *cyclic trimers* or just *trimers*) exhibit auxetic behavior, i.e. their Poisson's ratio is negative [7], when particles are highly anisotropic. It has been also shown that the presence of polydispersity increases the Poisson's ratio in the system [8].

This work is generalization of the two-dimensional (2D) model presented in Refs. [7, 8]. The aim of this study is to broaden our knowledge concerning the influence of microscopic structure and mechanisms on the macroscopic elastic properties of materials. The influence of such factors as molecular shape asymmetry and atomic size dispersion on the system's elastic properties is determined by computer simulations.

2 Model system

The studied system is 2D and consists of three-atomic molecules (trimers). For each molecule, the interacting sites (atoms), are placed at the vertices of an *isosceles* triangle. In this work it is assumed that the atoms interact through a purely repulsive potential of the form:

$$u_{ij}(d_{ij}, r_{ij}) = u_0 \left(\frac{d_{ij}}{r_{ij}} \right)^n,$$

where $d_{ij} = (d_i + d_j)/2$, d_i, d_j are the diameters of interacting atoms and r_{ij} is the distance between their centers. The exponent n is a parameter which describes the *hardness* of the potential (the potential tends to a hard-particle potential with increasing n), where its inverse, $1/n$, will be treated as the *softness* parameter. Atoms interact only with their nearest neighbors, i.e. interacting atoms share a side of their Dirichlet polygons. In the limit $n \rightarrow \infty$ the trimers can be thought of as *hard* bodies.

To obtain the structure of trimers built on isosceles triangles (see Fig 2), the molecules are aligned parallel to each other and oriented in the same direction, thus forming a *rectangular* lattice (see Fig. 3).

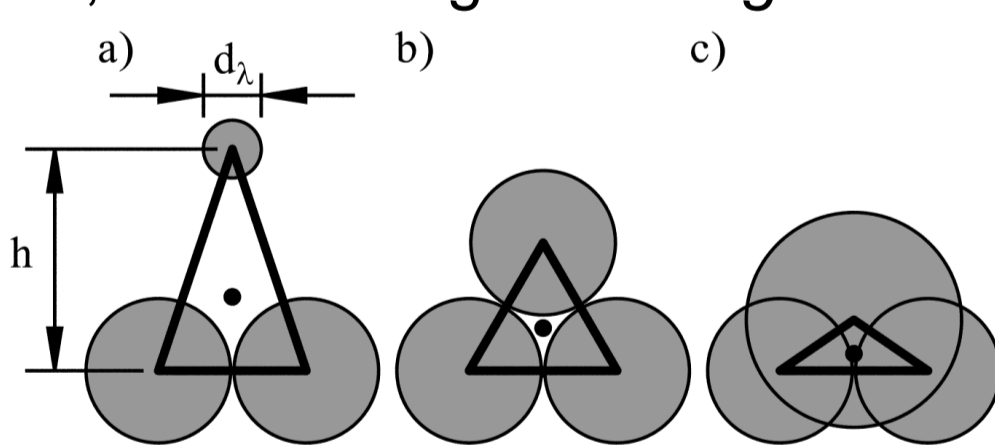


Figure 2. Shape of the trimer depending on the value of the asymmetry parameter, $\lambda \equiv d_u/\sigma$, where d_u is the diameter of the upper disc and σ is the diameter of the discs at the bottom of the triangle: a) $\lambda = 0.4142$, b) $\lambda = 1$ (perfect triangle of 3-fold symmetry axis) and c) $\lambda = 1.4773$.

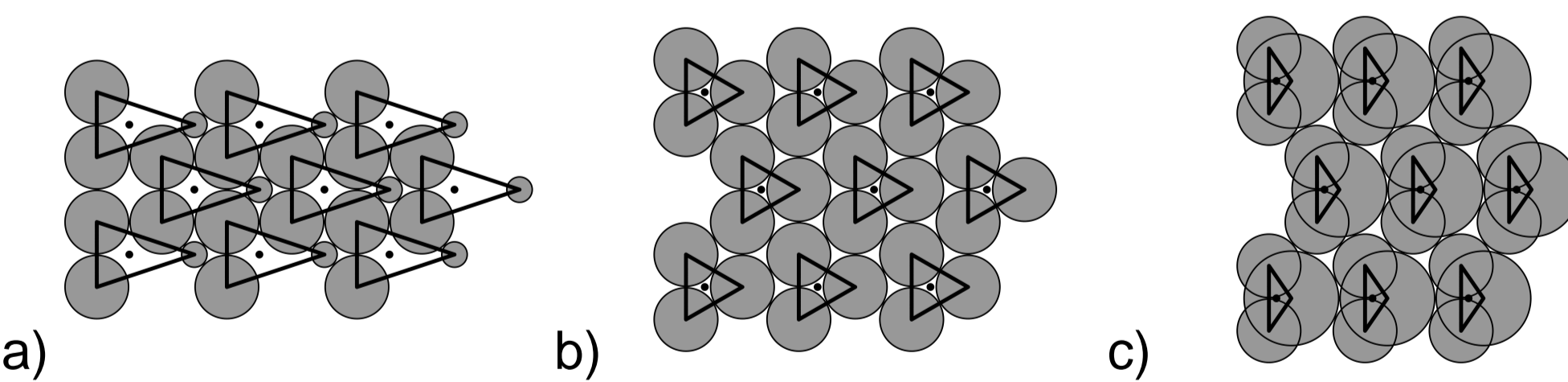


Figure 3. Examples of crystalline structures formed by molecules of extreme values of the molecular asymmetry parameter λ : a) $\lambda = 0.4142$, b) $\lambda = 1$ (isotropic structure) and c) $\lambda = 1.4773$.

2.1 Identical asymmetric trimers

Trimer asymmetry (see Figs. 2, 3) is due to the fact that the molecules are made on the basis of isosceles triangles and one of the molecule's atoms has the diameter,

$$d_\lambda = \lambda \sigma,$$

where σ is the diameter of the remaining two atoms and a unit length. The remaining two atoms are placed on the triangle's side also equal to σ . Thus, the molecular asymmetry parameter λ in the above formula scales the diameter d_λ of the third disc. It is worth noting that at close packing of hard trimers defined above and forming the lattice shown in Fig. 3, the possible values of λ can vary in the range of $(0.4142 \div 1.4773)$. For values of λ from outside this range the structure is unstable. In this work systems of λ from the range of $0.5 \div 1.3$ were studied, changing in 0.1 increments of λ . The system of $\lambda = 0.415$, close to the lower limit of λ , was also studied in order to investigate the extreme values of Poisson's ratio.

The height h of the isosceles triangle is a function of another asymmetry parameter w , defined as

$$h = wh_0,$$

where $h_0 = \sqrt{3}/2$, which corresponds to the height of the equilateral triangle of the side length equal to σ . w is related to λ by analytical formula presented in [9], where other details concerning the model and the computation method are also presented.

2.2 Trimers with atomic size polydispersity

In this case, the equivalent atomic diameters in the system are allowed to differ (slightly) from each other. Their values were generated according to the Gauss distribution function at a given standard deviation δ , which will be treated as the *polydispersity* parameter.

$$\delta = \frac{\sqrt{\langle d^2 \rangle - \langle d \rangle^2}}{\langle d \rangle}.$$

$\langle d \rangle$ in the above equation is the average diameter of the given kind of atoms. The diameters of equivalent atoms were generated in such a way that their averages matched the values of the corresponding systems of identical trimers. This allows one to keep the system energy close to the energy of the system without polydispersity which is important from the point of view of numerical accuracy of the computations. The following polydispersities were studied: $\delta = 0.003, 0.01$ and 0.03 for selected values of the molecular asymmetry parameter λ .

3 Basic formulae

In order to describe the elastic properties of an anisotropic system, exhibiting rectangular symmetry, it is convenient to use the formula describing the free enthalpy (Gibbs free energy) change, which is expressed as a function of the elastic constants B_{ijkl} of the system at non-zero pressure p and the Lagrange strain tensor ε_{ij}

$$\Delta G/V_{\text{ref}} = \frac{1}{2} \sum_{i,j,k,l} B_{ijkl} \varepsilon_{ij} \varepsilon_{kl},$$

where V_{ref} is the system's volume at equilibrium at the pressure p . The elastic constants are related to the elastic compliances tensor through the following formula [10]:

$$\sum_{m,n} S_{ijmn} B_{mnlk} = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) / 2.$$

The indexed delta symbol in the above equation is the Kronecker delta function. If we consider α as the direction of the applied infinitesimal stress change (the other components of the stress are kept unchanged) and β as the direction perpendicular to it (the direction in which we measure the material's response to applied load), we can express the Poisson's ratio as:

$$\nu_{\alpha\beta} = -\frac{S_{\beta\beta\alpha\alpha}}{S_{\alpha\alpha\alpha\alpha}}.$$

α and β are unit vectors defined as $\alpha = (\cos \phi, \sin \phi)$ and $\beta = (\cos(\phi + \pi/2), \sin(\phi + \pi/2))$, where ϕ is the angle describing the orientation of the vector α in the coordinate system defined by the crystalline axes of the system studied.

In 2D the Poisson's ratio depends, in general, on the direction of α . To describe the effective deformation of anisotropic media one can use the *average* Poisson's ratio $\langle \nu \rangle$ and *effective* Poisson's ratio ν_{eff} . By using the equation above and the formula $S_{\alpha\alpha\alpha\alpha} = \alpha_i \alpha_j \alpha_k \alpha_l S_{ijkl}$, they can be defined as:

$$\nu_{\text{eff}} = -\frac{\bar{S}_{\beta\beta\alpha\alpha}}{S_{\alpha\alpha\alpha\alpha}}, \quad \langle \nu \rangle = \frac{1}{2\pi} \int \nu_{\alpha\beta} d\phi.$$

Where $\bar{S}_{\beta\beta\alpha\alpha}, \bar{S}_{\alpha\alpha\alpha\alpha}$ are the components of the elastic compliance tensor averaged over all directions of α . In the results section the comparison of both, the effective and the averaged Poisson's ratios is presented.

4 Results and conclusions

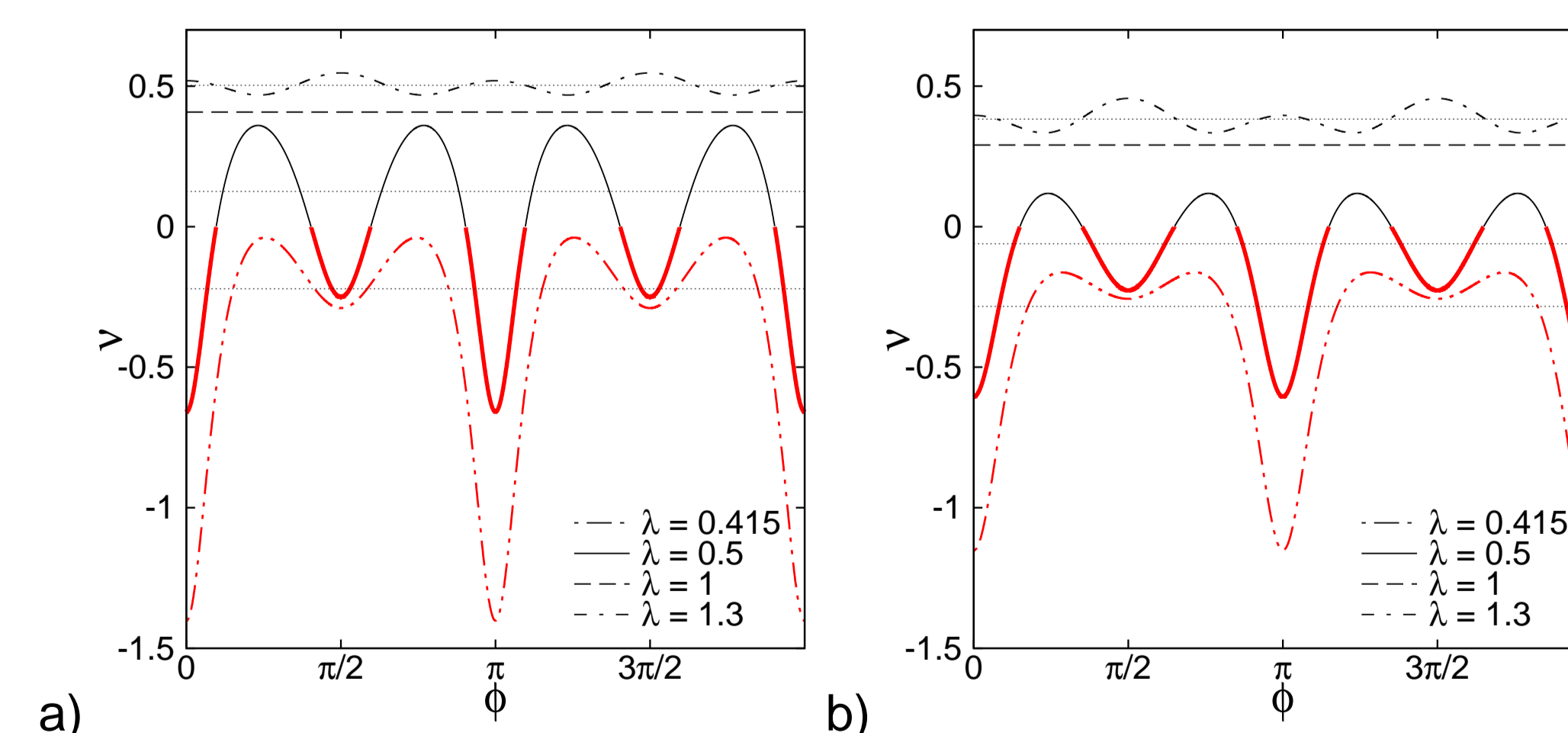


Figure 4. The Poisson's ratio dependence on the angle ϕ of the direction of applied deformation α , for different hardness parameter values a) $n = 5$, b) $n = 12$, c) $n = 768$. Parts of the curves in which the Poisson's ratio is negative are drawn with red lines, and the positive parts of the Poisson's ratio are drawn with black lines. Additionally for $\lambda \neq 1$, the effective Poisson's ratio, ν_{eff} , is marked with the thin dotted lines. Note that in the case when $\lambda = 0.415$, the Poisson's ratio in directions $\phi \approx 0, \pi$ drops below -1 .

The values of Poisson's ratio for systems with molecular asymmetry $\lambda \ll 1$ are **significantly lower** compared to the systems of symmetric molecules. In this case the Poisson's ratio is strongly angle dependent and highly negative, dropping **even below -1 for $\lambda = 0.415!$** The respective values of the Poisson's ratio for $\phi = 0$ are $\nu^{(n=5)} = -1.402$ and $\nu^{(n=12)} = -1.152$.

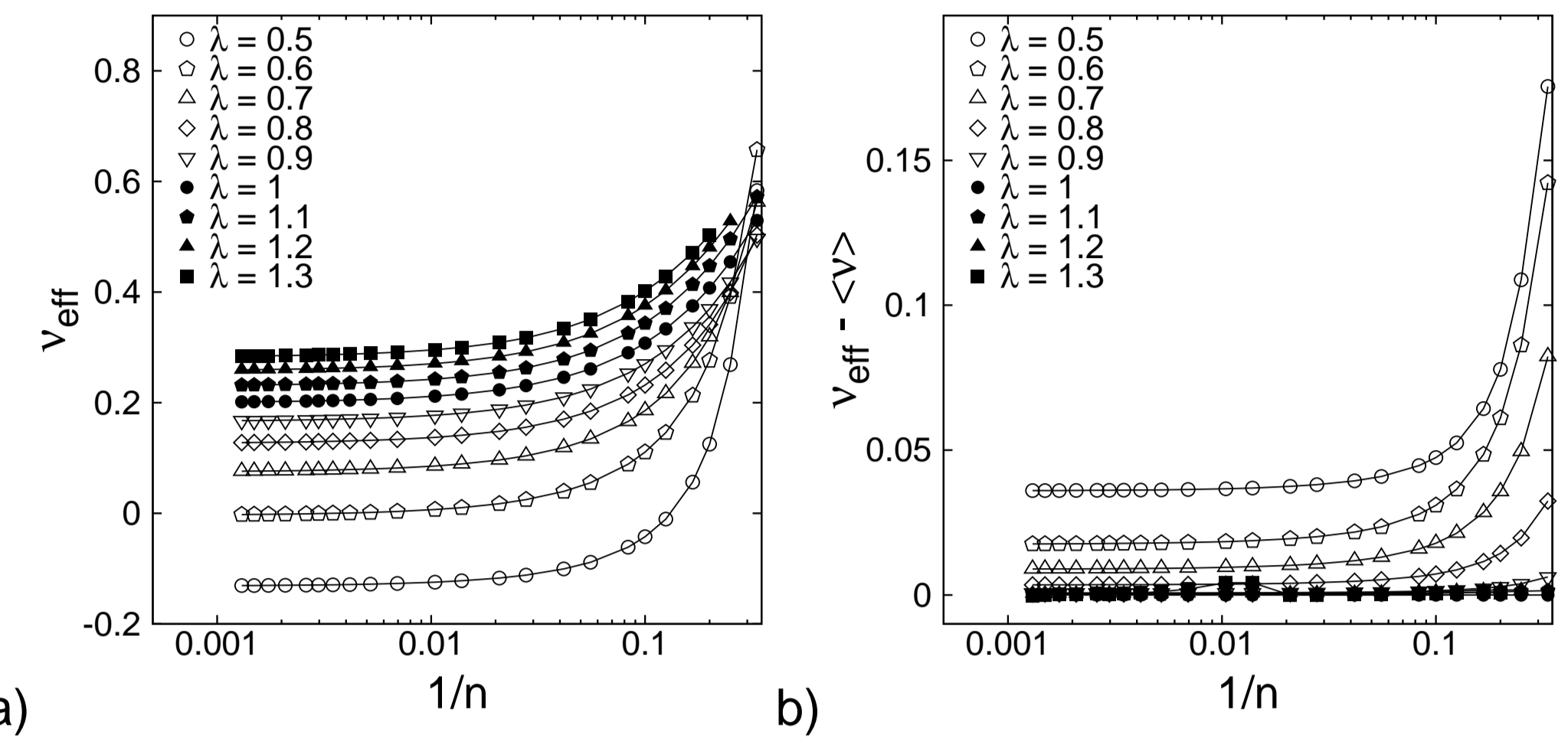


Figure 5. a) Effective Poisson's ratio shown as a function of the softness parameter for different values of the molecular asymmetry parameter λ and b) the difference between the effective and average Poisson's ratios. Solid lines are drawn to guide the eye.

The effective Poisson's ratio for crystal systems at different values of λ and its relation with the average Poisson's ratio are plotted in Figure above. As can be seen in the Figure 4, the Poisson's ratio for systems with $\lambda > 1$ depends on the deformation angle rather weakly. Looking at the structures in Fig. 3 one can see that molecules of $\lambda \gg 1$ are similar to discs. For this reason systems of $\lambda > 1$ become more isotropic than systems with $\lambda < 1$. There is **no significant difference** between the effective and average Poisson's ratios for high values of λ . In the case when $\lambda \ll 1$, the effective Poisson's ratio is always **negative**.

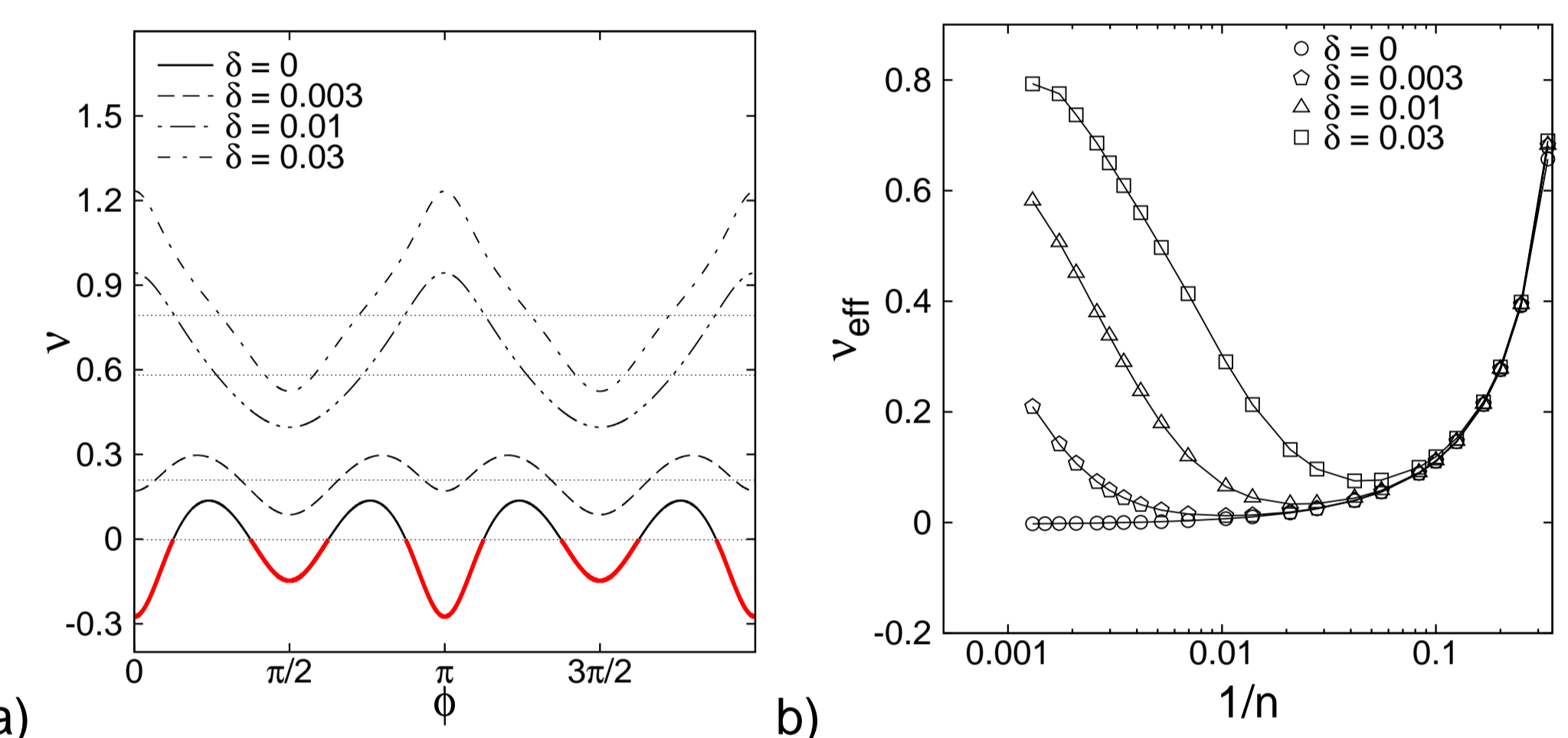


Figure 6. a) Poisson's ratio for polydisperse systems of $\lambda = 0.6$ and $n = 768$. Negative parts of the Poisson's ratio curve are drawn with thick red solid lines. Additionally, the effective Poisson's ratio is marked with thin dotted line for respective polydispersity values. b) The effective Poisson's ratio at $\lambda = 0.6$ as a function of the softness parameter.

The destructive, from the point of view of auxeticity, influence of disorder (atomic size dispersion) on elastic properties is presented above. **Poisson's ratio increases significantly with increasing δ and n** (in some directions by as much as $\Delta \nu \approx 1.5$), as was observed in the isotropic case [8]. With the increase of δ , Poisson's ratio becomes more and more dependent on the angle ϕ . The effective Poisson's ratio for the system at $\lambda = 0.6$ increased by $\Delta \nu_{\text{eff}} \approx 0.8$ in the case of the highest studied δ . As it can be seen, even as small amount of **disorder** as $\delta = 0.003$, **can eliminate auxetic behavior** completely. Thus, disorder introduced by atomic size polydispersity leads to increase of the Poisson's ratio in both isotropic [8, 11] and anisotropic systems.

Acknowledgements

Part of this work was supported by the Ministry of Science and Higher Education grants no. N202 07032/1512 and NN 202 1353 33. Part of the simulations was performed at the Poznań Supercomputing and Networking Center (PCSS).

References

- [1] R. S. Lakes, *Science* **238**, 551 (1987).
- [2] K. E. Evans, M. A. Nkansah, I. J. Hutchinson, and S. C. Rogers, *Nature* **353**, 124 (1991).
- [3] R. H. Baughman, J. M. Shacklette, A. A. Zakhidov, and S. Stafstrom, *Nature* **392**, 362 (1998).
- [4] K. E. Evans and K. L. Alderson, *Engineering Science and Education Journal* **9(4)**, 148 (2000).
- [5] R. H. Baughman, *Nature* **425**, 667 (2003).
- [6] K. W. Wojciechowski, A. Alderson, K. L. Alderson, B. Maruszewski, and F. Scarpa, *Physica Status Solidi (b)* **244**, 813 (2007), see also other papers in that issue and references therein.
- [7] K. W. Wojciechowski, *Journal of Physics A: Math Gen.* **36**, 11765 (2003).
- [8] J. W. Narojczyk and K. W. Wojciechowski, *Physica Status Solidi (b)* **244**, 943 (2007).
- [9] J. W. Narojczyk, A. Alderson, A. Imre, F. Scarpa, and K. W. Wojciechowski, in print (2008).
- [10] J. H. Weiner, *Statistical Mechanics of Elasticity* (Wiley, New York, 1983).
- [11] K. V. Tretyakov and K. W. Wojciechowski, *Physica Status Solidi (b)* **242**, 730 (2005).