Molecular simulation of molecular auxetic building-blocks

Final Report

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1. Introduction

Macroscopic auxetic materials are materials that display a negative Poisson's ratio. Nevertheless, their actual use is hindered by the fact that their specific morphology makes them materials with low density. To circumvent this drawback, it has been proposed to develop molecular auxetic units. No evidence of the very existence of such molecular unit has been raised so far. Simulations of auxetic molecules can be found in the literature, but as shown in this report, we have some concerns about their achievability.

The main question that must be addressed is the actual feasibility in synthesizing such auxetic molecular compounds. Some elements to answer this question will be brought forward in this report. Phase 1 of this work consisted of developing a multiscale simulation approach that would enable linking molecular structure to mechanical properties. This represents an essential step towards the synthesis of auxetic molecules. The resulting methodology should then be used in the subsequent Phase to design chemical structures that are candidates for the synthesis.

In order to develop the multiscale approach, the first step was to use the Discover code, from the Materials Studio environment, Accelrys®. Due to the specificity of auxetic compounds, additional codes in BTCL language have been written in order to complete the Discover code.

In the current report, deliverables consist of the protocol used to simulate the auxetic material properties under the Discover environment, including the new code written as a complement of the original software, and a proposition for a paper about the effectiveness of the mechanical equilibrium criterion in order to prepare simulation cells.

Calculation can be ultimately carried out in the LAMMPS environment, in order to take advantage of the CPU resources of the Mammouth supercomputer of Université de Sherbrooke. While developed under the Discover environment, the protocol is easily transferable to LAMMPS. Additional codes can also be easily written to become Unix-compatible.

2. Proposed approach

To make the most accurate link between properties computed at the atomistic level and the macroscopic properties, the state of simulated systems must be as close as possible to the conditions of the real system. In our lab, we thus developed a protocol based on the mechanical equilibrium criterion. At this state, pressure stemming from molecular interactions in the simulation cell compensates for the constraints brought by the simulation itself.[1] A consequence of this protocol is that the glass transition temperatures (T_gs) of a series of vinylic polymers and molecular glasses exhibit a linear relationships with experimental T_gs. Recently, we showed that it can be applied to anisotropic systems, such as liquid crystals. To support this, Phase 1 consists of applying this criterion to systems with hypothetical molecular auxetic units that are found in the literature. Hypothetical comes from the fact that no experimental density is available.

We thus applied first the procedure to amorphous polymers for which experimental Poisson's ratio data are available. It was then used to compute mechanical properties of the hypothetical auxetic molecules proposed in literature. This approach is sketched in Figure 1. Thanks to this procedure, we anticipate a robust protocol to assist the design of auxetic molecules.
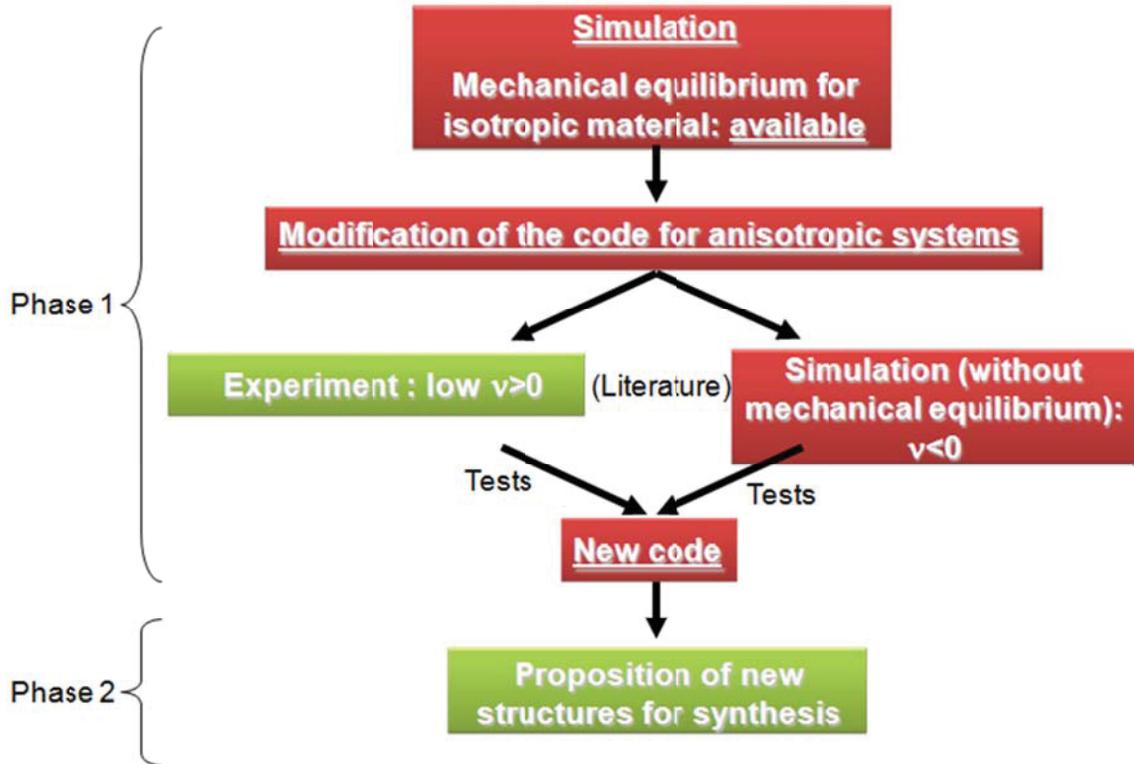
Figure 1. Proposed approach

3. Simulation protocol

The procedure to get reproducible values of the mechanical properties of polymers, in particular the Poisson's ratio, is proposed.

Step 1-Drawing/generation of the structures in a simulation cell with periodic boundary conditions (PBC), followed by a preliminary energy minimization according to particle coordinates.

For each amorphous polymer system, 40 structures were generated at 300 K, among which the 8 most representative ones were selected. Selection is based on 2 criteria: the radius of gyration of the configurations cannot depart too much from the average value; the classical energetic criterion.

Step 2-Heating/Cooling process

The selected configurations are heated from 300 K to 800 K by step of 50 K, with molecular dynamics (MD) simulation of 0.5 ns duration; in the NPT ensemble (number of atoms, pressure, and temperature are kept constant). The configurations are subsequently cooled back to 300 K in 20 K steps with MD of 1 ns duration.

Step 3-Compression/expansion procedure

This step is essential in the development of molecular auxetic compounds. Developed initially to treat mechanical properties of amorphous polymers, it was specifically applied to the studied systems. For amorphous polymers, the isotropic character must be preserved. Thus, a series of hydrostatic compressions/expansions, i.e. involving the complete volume independently of the cell directions, and energy minimizations according to atom coordinates was carried out [1]. For the network structures, anisotropy must be maintained. Thus, the compressions/expansions were performed according to each cell dimension. At the end of this stage, the configurations were found in a

mechanical equilibrium, leading to the following equalities: $\dfrac{\partial E_{potential}}{\partial V} = 0$ and

$\dfrac{\partial E_{potential}}{\partial q_i} = 0$.

Step 4-Stiffness matrix and Poisson's ratio

The static mechanical properties, Young's modulus (E), Bulk modulus (B), Shear modulus (G), and Poisson's ratio (ν) are computed from the Lamé constants extracted from the 6×6 stiffness matrix (C_{ij}) of each final configuration using the Discover code. For anisotropic network systems, the compliance matrix (S_{ij}) must be computed:

$S_{ij} = C_{ij}^{-1}$. The Poisson's ratio is then computed according to $\nu_{ij} = -\dfrac{S_{ji}}{S_{ii}}$ [2,3].

4. Additional code

In order to perform a series of compressions/expansions cycles along the three dimensions of a simulation cell, altogether for isotropic systems, and sequentially for anisotropic systems, a code has been written.

The current version of the code is given by two files, named *Compra_v3.bat* and *Compra_v3.in*. *Compra_v3.bat* is a script written in Windows batch file language that will be run under the Windows environment. This script calls the Discover engine to perform a calculation and determine the next action (compression or expansion, respectively) to apply, according to the result of the previous calculation. *Compra_v3.in* is a script written in BTCL language that will be executed by the Discover engine, according to the command it received from *Compra_v3.bat*. This script i) performs a

change in the box dimensions of the simulation cell, ii) carries out a subsequent energy minimization, iii) outputs a new simulation cell, and iv) tests if the computed potential energy is higher or lower than the potential energy stemming from the previous step. In step iv), if the computed energy is found lower, the same action, i.e. compression or expansion, is performed. If the new energy is higher, the following steps are completed:

1. The opposite action is performed to go back to the point of lower energy, the ensuing simulation cell becomes the reference.

2. Refinement. After step 1 is completed, the size of the compression/expansion increment (in Å) is decreased.

3. An expansion is carried out on the reference cell.

4. A compression is performed on the reference cell.

The energies of steps 2 and 3 are compared in order to choose the next action to achieve. In step 2, the refinement increments through the compressions/expansions process are 0.1, 0.05, 0.01 and finally 0.005 Å.

In *Compra_v3.bat*, the name of the original simulation cell on which the calculation are carried out (**.car* and **.mdf*) must be provided as a user input. User must also specify if the simulated system is isotropic or anisotropic. In *Compra_v3.in*, the cut-off, force field and maximum number of optimization steps must be given as user inputs. The parameters of the compressions/expansions, i.e. the step dimension in Å and the order in which the cell dimension are changed, as well as other calculation parameters can also be modified in this file. Both files contain comments between lines of codes.

5. Studied structures

The selected structures were of two kinds. The first kind was amorphous polymers whose experimental Poisson's ratio is known. It corresponds to a validation stage that is prerequisite in simulation. The second kind was networks whose structures come from literature. They have already been simulated, and, according to the authors of the publications, are potential candidates to exhibit auxetic behavior. They argued that such structures are 2D networks that mimic known auxetic macroscopic structures. The very same protocol will be applied on various structures of each kind.

Studied polymers

The studied amorphous polymers are poly(methylmethacrylate) (PMMA) and two members of the poly(glycol methacrylate) family. The PMMA was studied in reference [1] and experimentally display a Poisson's ratio around **0.32-0.4** [7]. The poly(triethylene glycol dimethacrylate) experimentally displays a very small Poisson's ratio for a polymer, around **0.2** [7]. It is among the lowest ν a polymer can exhibit without any imposed shape manipulation. This polymer (Figure 4) is highly reticulated. The poly(tetraethylene glycol methacrylate) (Figure 4) is another polymer from the poly(glycol methacrylate) family, and displays a Poisson's ratio around **0.5**.[8] From a simulation perspective, they are interesting to study since they share exactly the same force field parameters. An accurate representation of the difference in the Poisson's ratio indicates that molecular environment is well characterized, and valid conclusions can be achieved.

Hypothetical auxetic molecular structures

The first structure that was simulated was the 'classical' molecular re-entrant honeycomb reflexyne structure proposed by Evans [4] and displayed in Figure 2. Grima et al. [5] used molecular mechanics with the *pcff* force field and PBC. A commercial software package Cerius2 from Accelrys® was used. Two stresses have been applied, on-axis and off-axis (45°). The aim was to gain insights into the molecular level deformations which result in auxeticity. Poisson's ratios were computed from the compliance matrix obtained through the second order derivative of energy with strain. Values of **-0.31** in one direction of the plane and **-0.46** in the other, have been computed for the re-entrant honeycomb structure of Figure 2 (REH_Evans).
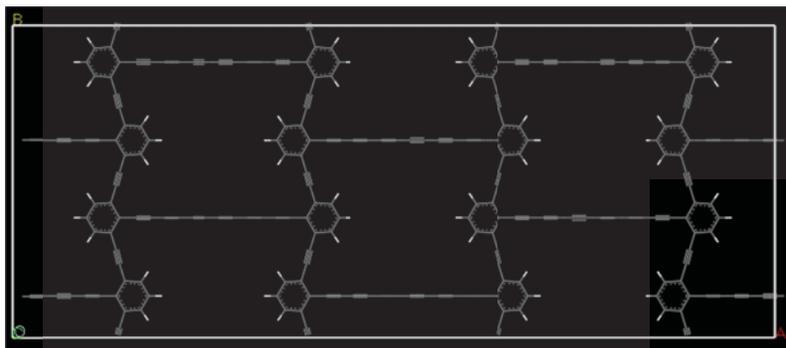
Figure 2. The 'classical' molecular re-entrant honeycomb structure of Evans

The second and third networks stemming from literature, which are the subject of this report, are similar to the previous one, and are still based on the re-entrant mechanism. The structures are alternating copolymers that are proposed to self-assemble through hydrogen-bonding (Figure 3) under specific conditions [6]. If the self-assembly process experimentally occurs, it should give rise to a potentially more synthesis-friendly route to achieve a molecular auxetic lattice. Wei et al. thoroughly studied 19 members of the

family depicted by Figure 3. Two compounds were selected for this work: (junction I/(NH-Ph)$_3$-NH) and (junction II/NH-(Ph)$_2$-NH), named REH_DA1 and REH_DA2 in the present report, respectively. Those structures were chosen since the latter displays one of the best auxetic behavior of reference [7]. This behavior is significantly different from that of the former. It has to be pointed out that the two structures share the same force field parameters. The Dreiding force field with PBC was used, and calculations have been carried out in the Cerius2 environment from Accelrys®. Computed Poisson's ratios in the plane of Figure 3 are **-0.1242/-0.0749** and **-0.3416/-0.2349**, respectively.

Figure 3. Two structures of molecular re-entrant honeycomb with 'double arrow': REH_DA1 (left) and REH_DA2 (right).

Figure 4. (left) triethylene glycol dimethacrylate repeat unit and (right) tetraethylene glycol methacrylate repeat unit.

6. Results

The force field used in our studies is Compass. It is of 2nd generation and has been developed to accurately represent non-bonding interactions. Moreover, to highlight the

pertinence of using the compression/expansion step, results with and without applying it are compared.

Polymers

We conducted simulations on poly(methylmethacrylate) (PMMA) and poly(tetraethylene glycol methacrylate) (PTGM). The simulation protocol, described in paragraph 3, has been applied to each polymer. The static mechanical properties averaged over the 8 configurations are shown in Table 1.

Table 1. Computed Poisson's ratio for a system of PMMA and PTGM, without and with the compression/expansion (C/E) procedure.

Polymer		without C/E	with C/E	Exp. [7]
PMMA	E (GPa)	-2 ± 40 (8 conf.) $\qquad$ 10 ± 5 (2 conf.)	4.4 ± 1.0 (5 conf.)	~ 2-3
	G (GPa)	12 ± 41 (8 conf.) $\qquad$ 50 ± 66 (2 conf.)	1.6 ± 0.4 (5 conf.)	~ 1-2
	υ	0 ± 6 (8 conf.) $\qquad$ 0.4 ± 0.4 (2 conf.)	0.31 ± 0.08 (5 conf.)	~ 0.3-0.4
PTGM	E (GPa)	9 ± 37 (8 conf.)	6.4 ± 1.1 (5 conf.)	
	G (GPa)	16 ± 76 (8 conf.)	2.2 ± 0.4 (5 conf.)	
	υ	0 ± 1 (8 conf.)	0.34 ± 0.11 (5 conf.)	~ 0.5

From Table 1, it is observed that for PMMA, over the 8 configurations, only 2 comply with the positive strain energy under load criterion, and only one for PTGM [3]. This criterion states a list of conditions that the elements of the compliance matrix of a material with orthorhombic symmetry, must satisfy at equilibrium. The value averaged over the 2 configurations of PMMA that satisfy this criterion, was therefore also shown

in Table 1. On the other hand, for each polymer, 8 simulations cells were subjected to the compression/expansion script previously discussed. In both cases, after the use of the procedure, 5 configurations over the 8 satisfy the positive strain energy under load criterion. A significant increase in the overall quality of the cells must be outlined. The averaged values over these 5 configurations are also displayed in Table 1. A comparison of the data with and without our compression/expansion procedure is readily seen. Standard deviation values are remarkably reduced and average values are significantly closer to the available experimental data.
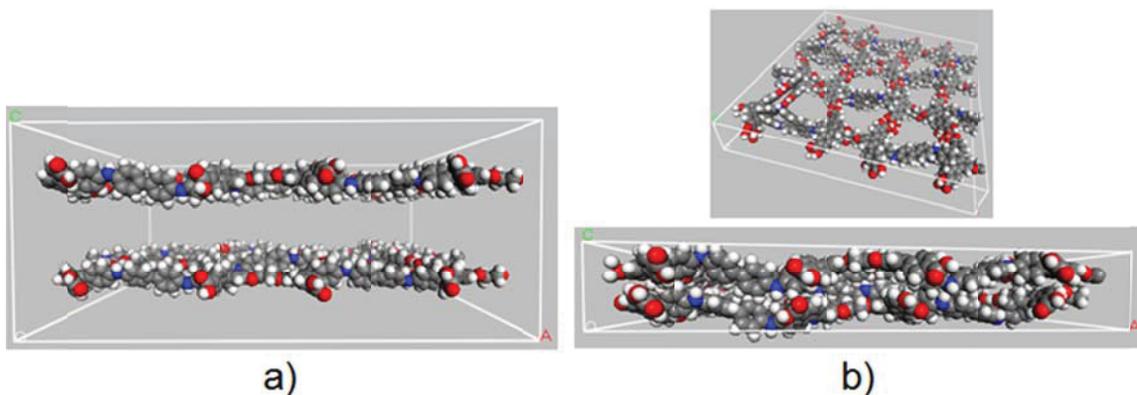
Figure 5. A simulation cell containing the theoretically auxetic molecular pattern REH_DA2, (a) before and (b) after the anisotropic compression/expansion procedure.

Hypothetical molecular auxetic structure

Literature provides us with molecular units that, according to calculations, must yield auxetic property. We have selected three examples: the text-book re-entrant honeycomb from Evans et al. (REH_Evans) [4] and two double-arrow re-entrant honeycomb from Wei et al. (REH_DA1 and REH_DA2) [6]. For each structure, the authors did not reach the mechanical equilibrium state. Put in other words, they did not use the

compression/expansion protocol. This protocol we developed has shown its relevance in computing mechanical properties. Applying it to the hypothetical molecular auxetic units gives structures whose shape is very different from the initial ones, as seen in Figure 5. Molecules are shown before and after the anisotropic compression/expansion procedure, in Figure a) and b), respectively. Accordingly, these structures will lead to different values of mechanical properties, and more specifically different Poisson's ratios, as observed in Table 2.

Table 2. Computed Poisson's ratio for a theoretically auxetic molecular pattern, without and with the compression/expansion (C/E) procedure.

Polymer		without C/E	with C/E	Calc.
REH_Evans [4,5]	E_x / E_y (GPa)	81.5 ± 5.5 / 82.4 ± 4.1	90.4 ± 2.1 / 51.6 ± 0.9	114.28 / 78.40
	G_{xy} (GPa)	3.2 ± 0.6	0.50 ± 0.07	2.75
	$\upsilon_{xy} / \upsilon_{yx}$	-0.22 ± 0.02 / -0.25 ± 0.05	-0.82 ± 0.02 / -0.47 ± 0.01	-0.46 / -0.31
REH_DA1 [6]	E_x / E_y (GPa)	13.6 ± 0.6 / 2.6 ± 0.5	17.4 / 9.6	33.26 / 20.06
	G_{xy} (GPa)	-0.04 ± 0.06	0.18	
	$\upsilon_{xy} / \upsilon_{yx}$	0.16 ± 0.44 / 0.02 ± 0.03	-0.26 / 0.24	-0.12 / -0.07
REH_DA2 [6]	E_x / E_y (GPa)	20.8 ± 0.4 / 8.6 ± 0.1	7.2 ± 2.8 / 14.0 ± 4.1	18.41 / 26.78
	G_{xy} (GPa)	0.08 ± 0.11	0.28 ± 0.14	
	$\upsilon_{xy} / \upsilon_{yx}$	0.102 ± 0.048 / 0.054 ± 0.002	-0.15 ± 0.08 / -0.25 ± 0.25	-0.23 / -0.34

For each structure, a simulation cell has been built and has been subsequently energetically minimized according to the position of the particles. To obtain 8 different

configurations for each REH structure, the original cells were submitted to a 1 ns molecular dynamics, and configurations were extracted each 100 ps over the last 0.7 ns. The static mechanical properties were computed on these configurations. Among these configurations, the 1, 0 and 2 configurations for REH_Evans REH_DA1 and REH_DA2, respectively, complied with the positive strain. Average values over the 8 configurations are shown in Table 2. The configurations were submitted to the anisotropic compression/expansion procedure. The number of configurations with positive strain among the 8 ones, increased for each molecule: 7 and 4 for REH_Evans and REH_DA2, respectively. Conversely, only one configuration filled this criterion for REH_DA1. Since no standard deviation can be associated with this molecule, it was considered as not reliable.

Considering the REH_Evans structure, the results stemming from the procedure predict a stronger auxetic behavior than the published data. In the case of the REH_DA2 auxetic unit, auxeticity is predicted to be lower than the literature value. The important corollary of these observations is that the auxetic potential of the proposed materials cannot be readily compared among groups. We acknowledge that the development of this field is in its infancy and still far from the theory to laboratory transition. Nevertheless, we argue that the use of precise benchmark, such as the achievement of mechanical equilibrium, is an essential asset. Moreover, this study gave us the opportunity to reveal that the current process in designing auxetic molecular units is not appropriate. It was based on a simple imitation of the macroscopic auxetic units. This Top-Down approach is far from straight forward. Conversely, the Bottom-Up perspective has clearly demonstrated its great potential in proposing new materials. There are numerous factors that can explain the

failure of a simple homothetic translation from macroscopic shape to microscopic structure. The main reasons are the strength of interactions, the free volume, the entropic character, the thermal agitation, to name a few. Accordingly, a different and new strategy must be developed.

7. Conclusions and perspectives

This report marks the beginning of a very interesting study on molecular auxetic compounds. It is the results of 2 years of study on the most pragmatic approach which consists in mainly reproducing existing data. These data are experimental, stemming from 2 polymers, and computational, coming from hypothetical molecular auxetic units. The first conclusion was that this study emphasizes the role of the compression/expansion procedure to compute mechanical properties. This procedure efficiently enables the accurate computation of mechanical properties, in particular Poisson's ratio, of polymers. The present report thus argues that the compression/expansion procedure is effective in its present version.

The second conclusion is that a different procedure than mimicking the macroscopic auxetic structure must be definitively followed. An interesting avenue found in the literature has been proposed by Aldred et al. [8]: a polymer containing swivelling mesogens has been designed. This family of compounds relies less on a mechanical deformation scheme, inherited from the macroscopic realm, and more on a molecularly assessed change in the packing of the molecules. A second route is to perform simulation at the mesoscale level of auxetic structures. This step is crucial since it is the link

between nanoscopic structure where auxetic architecture was found to exist, and atomistic domain where there are no proofs of any existence of auxetic unit. If auxetic structures are found at the mesoscopic scale, a route will then open for discussions with organic chemists to find the best organic candidates that respond to this specific architecture. This endeavour has never been done.

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