

Modelling the basic components of rubber-like materials

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Abstract: Elastic materials are usually composed of long polymeric entangled chains of organic elements, typically understood as complex networks that can be stretched. This paper presents a theoretical study of a network described as an ensemble of polymer sections, each one modelled as a non-interacting attractive spring with constant k fixed at one spring-end and subjected to a force F at the other end. An analytical solution of the model in the canonical ensemble is presented. Monte Carlo simulations are also carried out for different values of temperature and tensile force. Then, an extensive analysis of the trends of thermodynamic magnitudes is exposed. The found qualitative behaviours are studied and compared with the experimental and theoretical results in the literature. A final proposal to add interactions into the model is discussed.

I. INTRODUCTION

Elastomers are materials composed of polymers, stretchable long chains of molecules typically formed of organic elements [1]. This kind of materials are attracting a lot of attention thanks to their promising properties, such as elasticity, low costs, and room temperature transformations. For example, one of the most novel applications is based on the so-called elastocaloric effect (eCe), which consists on a sudden increase in temperature of the material after an adiabatic stretching [2], partly due to Strain-Induced Crystallization (SIC) [3]. The inverse effect can also be induced, i.e., a temperature decrease after unstretching. This phenomenon could be the basis for environmentally friendly cooling applications [4]. In addition, the process of vulcanization, that is, cross-linking different polymer sections by adding elements such as carbon to a sample has shown to enhance the eCe of elastomers [3], as well as some mechanical properties including rigidity and durability. Wide experimental and theoretical research focused on these and many other topics based on elastomers have been and is continuously being carried out.

A thermodynamic description of these systems have been elaborated [5], exposing other interesting features. For instance, when the temperature of natural rubber subjected to a constant tensile stress increases, it contracts in the direction of the applied force, i.e., it reduces its length [6]. This reflects the presence of an elastic force that opposes the external force that stretches the polymer, which may be counter-intuitive. For example, ideal gases, a very familiar system, always expand in all directions when their temperature increase. This will be a fact, among others, that will be treated in the present study. The properties of elastic materials described so far are complex and fascinating and have awakened the interest of condensed matter physicists.

An appropriate physical image of rubber-like materials is a 3-dimensional network of long polymer chains of different lengths linked by a given number of nodes, i.e. cross-links [1, 7]. It is not easy to propose a theoretic

cal and microscopic model for such a challenging problem. The objective of this study is to tackle the problem at a fundamental level to enhance the understanding of rubber-like materials within a comprehensible vision. Part of the complexity of the problem could be taken into account by considering that every chain between the nodes is an attractive spring, given the elastic behaviour of polymeric chains [7]. The aim of this study is, however, to investigate the fundamental unit of this model. Considering initially a network of polymeric chains, a single section is isolated and modelled as a spring fixed at one end, as shown in Fig. 1 (a). The other extreme is free to fluctuate thermally. The isolated spring is then subjected to an external force F , which will allow the description of stretching and some related properties mentioned above.

This way of approaching the problem by focusing on its elemental component is, of course, a simplification. Making an analogy to magnetic materials or gases, it could be thought as if one single spin or atom was studied

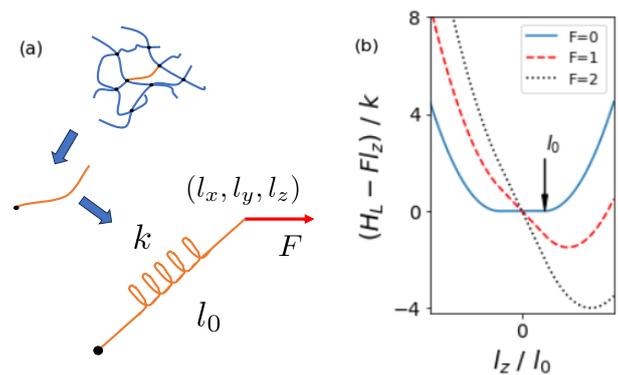


Figure 1: The studied system corresponds to an isolated polymeric chain of a 3-dimensional network of polymers. It is modelled as an attractive spring of elastic constant k , and natural length l_0 . One of its ends is fixed, while the other one is subjected to a force F (a). Spring potential for different values of F plotted for $l_x = l_y = 0$ in terms of l_z (b), as given by Eq. 2

in order to understand their basic behavior, respectively. However, there is a fundamental difference, which is that here the polymeric chain does perceive its own elasticity described by a potential containing only an attractive component, see Fig 1(b).

In short, in this work an ensemble of many independent springs that represent the polymer sections constituting elastomers are studied and their thermodynamic features are evaluated, in order to understand the fundamental behaviour of polymers with a simple and intuitive picture. Firstly, in section II A an analytical solution in the canonical ensemble is presented and Monte Carlo (MC) simulations are performed in section II B. Further investigations could be done by interconnecting the springs, that is, adding interactions between polymer sections, and exploring if this more sophisticated model agrees well with known experimental results, which is discussed in section II C. The paper finalizes with the conclusions in section III.

II. STATISTICAL MECHANICS OF NON-INTERACTING ATTRACTIVE SPRINGS

A. Analytical model

One of the main advantages of this simplified model, with non-interacting springs, is that it corresponds to a 1-body problem, so it can be solved analytically. Consider a spring of natural length l_0 and elastic constant k with one fixed end (representing a node within the polymeric network) and the other one free to thermally fluctuate in three dimensions (Fig. 1). The latter is subjected to an external force F that is taken parallel to the z axis and that stretches the system. For a given point in the phase

space, the length of the spring is $l = \sqrt{l_x^2 + l_y^2 + l_z^2}$. The spring response is modulated as an attractive elastic force that only acts if $l > l_0$. It is in thermal equilibrium at a temperature T . A statistical treatment in the canonical ensemble corresponding to this situation is going to be exposed now. The Hamiltonian of the system may be written as

$$\mathcal{H} = \frac{p^2}{2m} + H_L - Fl_z, \quad (1)$$

H_L being the term for the elastic potential energy:

$$H_L = \begin{cases} 0 & \text{if } l \leq l_0 \\ \frac{1}{2}k(l - l_0)^2 & \text{if } l > l_0, \end{cases} \quad (2)$$

see Fig 1(b). Its partition function is thus given as:

$$Z = \int_{\Omega} e^{-\beta\mathcal{H}} d\Omega, \quad (3)$$

where $\beta = \frac{1}{k_B T}$ is the Boltzmann factor. This expression can be calculated by breaking the whole integral into an integral of moments and the integral in the position coordinates (l_x, l_y, l_z) , both written in spherical coordinates, $Z_P = (2\pi m/\beta)^{3/2}$, and

$$Z_L = \frac{4\pi}{\beta F} \int_0^{\infty} dl e^{-\beta H_L} l \sinh(\beta Fl) = \frac{4\pi}{\beta F} I_{s1}, \quad (4)$$

respectively. The notation of this integral in terms of I_{s1} is given because the latter appears again in some other important expressions. The “s” sub-index denotes $\sinh(\beta Fl)$ (it would be a “c” for a cosh) and the 1 refers to the power of l . The partition function obtained is:

$$Z = \left(\frac{2\pi m}{\beta}\right)^{3/2} \left\{ \cosh(\beta Fl_0) \left[\frac{l_0}{F\beta} + \sqrt{\frac{\pi}{2\beta k}} \frac{e^{\frac{\beta F^2}{2k}}}{k} \left(F + kl_0 \operatorname{erf} \left(\sqrt{\frac{\beta F^2}{2k}} \right) \right) \right] \right. \\ \left. + \sinh(\beta Fl_0) \left[\frac{1}{k\beta} - \frac{1}{(\beta F)^2} + \sqrt{\frac{\pi}{2\beta k}} \frac{e^{\frac{\beta F^2}{2k}}}{k} \left(kl_0 + F \operatorname{erf} \left(\sqrt{\frac{\beta F^2}{2k}} \right) \right) \right] \right\}.$$

From here the Helmholtz free energy and the entropy of the single spring could be computed. However, this study focuses on the expected values in the different directions, given by:

$$\langle A \rangle = \int_p dp^3 \int_l dl^3 \frac{e^{-\beta\mathcal{H}}}{Z} A. \quad (5)$$

As one could expect, there is no mean displacement in the directions perpendicular to the axis of the applied force, i.e., $\langle l_x \rangle = 0$ and $\langle l_y \rangle = 0$. Other calculated expected

values are:

$$\langle l_z \rangle = \frac{1}{\beta F I_{s1}} (\beta F I_{c2} - I_{s1}), \quad (6)$$

$$\langle l_x^2 \rangle = \frac{1}{(\beta F)^2 I_{s1}} (\beta F I_{c2} - I_{s1}), \quad (7)$$

$$\langle l_z^2 \rangle = \frac{1}{(\beta F)^2 I_{s1}} ((\beta F)^2 I_{s3} - 2\beta F I_{c2} + 2I_{s1}). \quad (8)$$

These expressions are important because they give, for instance, an estimation of the volume of the system. Notice that the expected values remain in terms of some integrals that repeat themselves in the expressions. These integrals have been determined analytically. For more details see the Annex. The corresponding functions, as represented in Fig. 2, are compared with respective MC simulations. In the following section we develop the latter and discuss the results altogether.

B. Monte Carlo simulations

Monte Carlo simulations implementing the Metropolis algorithm of the considered attractive spring have been also carried out. First, these simulations can be used as a numerical test for the analytical solutions obtained in the previous section. In addition, they open the opportunities to further research. It is important to highlight that here only an ensemble of independent springs is considered, ignoring interactions between them. Nevertheless, a future aspiration is to connect them, as well as being able to take into account a set of non-identical springs (different values of l_0 , k , and considering interactions). The written MC code lays out the groundwork for such future developments.

In particular, in this paper simulations of $\approx 10^6$ MC steps using the pseudo-random generator MT19937 [8] have been executed for each reduced temperature $T^* = k_B T$ and F . It is important to highlight that it has been imposed that $l_0 = 1$ and $k = 1$. These values define the length and energy scales of the problem, so the range of values of the temperature T^* and F have been chosen taking this into account accordingly. Thereafter, all the graphs have been plotted normalizing the length value by l_0 and the energy or force magnitude by k . The acceptance ratio for the MC steps has been controlled by adapting the value of the proposed change of the thermally fluctuating position. The acceptance has been forced to be between 0.6 and 0.9.

The written program allows to perform MC simulations for different values of T^* and F for the spring; simulating a loop in T^* for a fixed F , or a loop in F for a fixed T^* . The initial considered conditions are $l_x = l_y = l_z = 0$ at each MC step. The not-fixed spring-end is subjected to a force F and fluctuates thermally. Consequently, a family of curves in terms of (F, T^*) is obtained. The results of the trends of the executed values for $T^* = 1$ are shown in Fig. 2. The chosen value of T^* is reasonable for two reasons. First, it agrees with the mentioned energy and length scales. This has been verified using the analytical expressions. Second, the maximum values of $l_z/l_0 \approx 5$ are plausible, since there is wide experimental evidence showing that these materials can be stretched perfectly up to five times, or even more, its initial length [3].

It can be observed in Fig. 2 that the analytical solutions represented in black lines perfectly match with the computational results for all the expected values, which

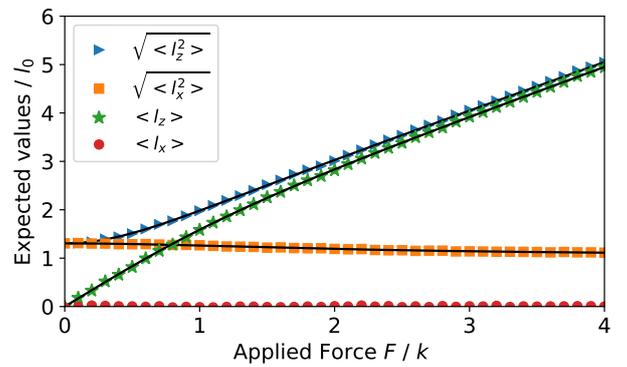


Figure 2: Expected values of the mean displacement and the mean square displacement in the different directions. z is the direction of the applied force. The results shown correspond to $T^* = 1$. The color dots represent the MC results, while the straight black lines correspond to the analytical solutions for each magnitude.

validates the numerical calculations. From now on, all the simulation behaviours will be discussed.

Firstly, one may notice that, as expected, there is no mean displacement in the directions perpendicular to the applied force: $\langle l_x \rangle = \langle l_y \rangle = 0$. By contrast, the mean square displacement in these directions $\langle l_x^2 \rangle = \langle l_y^2 \rangle$ is non-zero. The obtained tendency is that it decreases when the applied force increases. This phenomenon corresponds to a reduction of the width of the sample when stretched, as its length increases. Fig. 3(a) shows the relative value of the components perpendicular to the force (x) with those parallel to it (z), for different temperatures. The system size increases along the direction parallel to the applied force, while the perpendicular section reduces, as typically observed in systems under uniaxial stress. All the plotted curves tend to 0 for large values of F , but their decay is more gentle (less abrupt) as T^* increases,

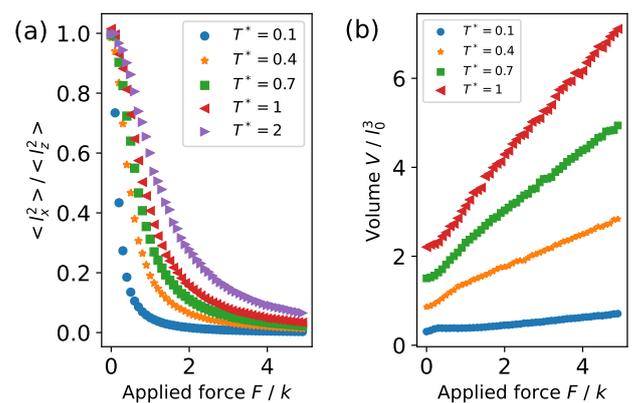


Figure 3: Plot of the obtained curves of $\langle l_x^2 \rangle / \langle l_z^2 \rangle$ in terms of the external applied force F for different temperatures T^* (a) and representation of the evolution of the estimated volume (b).

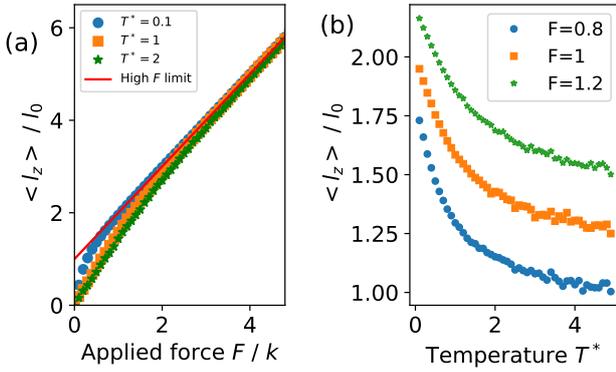


Figure 4: Evolution of the elongation $\langle l_z \rangle$ in terms of the applied force when the spring is at different temperatures (a), and in terms of T^* for constant F (b).

owing to a greater influence of the thermal fluctuations (the entropic contribution).

It is worth pointing out that the conservation of volume was one of the main assumptions made by Flory to deduce the equation of state for rubber-like materials. The paper written by this author in 1939 is one of the most important references in this research field [9]. Here, Flory predicted the SIC and calculated the entropy change associated with this phenomenon. Apart from the fact of being a condition for his theoretical studies, the conservation of volume has been also observed experimentally for different materials, those having a Poisson ratio of $\nu = \epsilon_{trans}/\epsilon_{axial} = 0.5$ being ϵ the strain along the indicated direction.

The simulation does not show a conservation of the volume, whose estimation has been taken as $V = \sqrt{\langle l_x^2 \rangle \langle l_y^2 \rangle \langle l_z^2 \rangle}$, as shown in Fig. 3(b). The most reasonable explanation for this disagreement may be the following. Since the considered ensemble of identical springs is a simplification, it assumes that the exerted force is the same for all of them. Nevertheless, in reality, when a polymeric network is stretched, not all the sections feel the same force owing to the disordered geometric distribution in polymers. This could be tested in the future by adding a geometric factor to the code, which would require further theoretical analysis.

The next step is to examine in greater detail the behaviour along the direction z in which the external force that stretches the polymer has been applied. $\langle l_z \rangle$, the length along the stretched direction, is a parameter of elongation. It can thus be regarded that $\langle l_z \rangle$ describes the strain of the system in this direction, whereas the tensile force F is the stress.

First, note that Fig. 4(a) shows that the usual Hooke linear relation between the elongation $\langle l_z \rangle$ and the force F is satisfied in the limit of high values of F , when the chain is fully taut. Indeed, when the polymer section is stretched with an external force F , its reaction is an opposite elastic force: $F_{react} = -k(l_z - l_0) = -F$. This

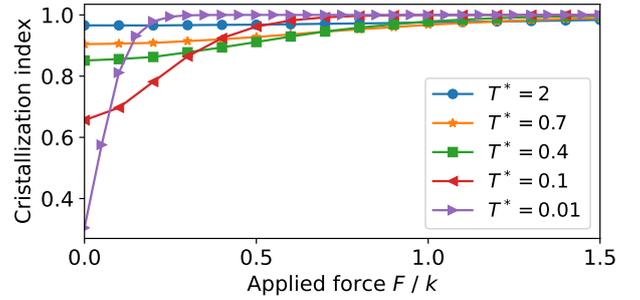


Figure 5: Crystallization index evolution in terms of the external applied force at different values of T^* .

expression turns into $l_z = F/k + l_0$ which is precisely the indicated straight red line that overlaps the computational data in the limit of large F .

Another interesting feature can be noticed. If a value of the force is taken and a vertical line is traced from there, the first curve that will be intercepted is the one corresponding to $T^* = 2$ (the largest T^* in this graph), which means that, for a constant F , a lower value of $\langle l_z \rangle$ is found for a higher temperature T^* . In order to understand this relation in a clearer way, $\langle l_z \rangle$ is also plotted in terms of T^* for different constant applied forces F in Fig. 4(b). The MC noise that can be perceived in Fig. 4(b) could not be smoothed out by increasing the number of MC steps up to $3 \cdot 10^6$, but it does not affect the next qualitative discussion. Indeed, the elongation $\langle l_z \rangle$ decreases with temperature, when the external force remains constant in the polymer. This is, therefore, a phenomenon of contraction in the longitudinal direction (z axis) when T^* is raised for a constant F [6], and follows from the entropic forces that appear in this sort of materials when they are stretched. From a general point of view, polymers want to contract in order to increase their entropy, since the conformation entropy of a polymer in its amorphous, random-coiled state is bigger than in the extended (e.g. crystalline) state due to a larger number of available configurations or micro-states.

SIC is the phase transformation of polymers from an amorphous state to a crystalline state when they are subjected to a tensile stress. In the crystalline phase, polymer chains are taut and highly oriented in the direction of the applied force. It has been widely studied experimentally [10] and is one of the contributions to the eCe [3]. The crystallization index (CI) is defined as the fraction of polymer chains that are taut. Fig. 5 shows the evolution of the CI when applying a force for the studied system. It has been computed by counting the number of times that the simulated spring is tensed throughout the MC steps. Note that for large values of F all the chains are completely aligned, as it has to be (limit $CI \rightarrow 1$). Moreover, the CI decreases at lower T^* and $F = 0$. This is ascribed again to the contribution of thermal fluctuations. Certainly, at low T^* , the only way of increasing CI is via the application of an external force.

C. Future work concerning the addition of interactions

The model described above is a simplification because it does not account for the interactions between different springs. Here every polymer section was represented by an independent spring that feels only its own elasticity. Moreover, identical values of l_0 and k for the springs have been considered (similar to an Einstein model). In a real network, a number of sections are connected to two cross-links (Fig 1(a)), in a way that they feel the influence of their neighbouring chains. It is also unrealistic to assume the same values of l_0 and k for all the polymeric sections, given the randomness of the distribution of nodes created by the vulcanization process. There is a large number of options to take these facts into account.

One possibility would be to consider a system with a random distribution of a given number of cross-links, with springs between them. Some conditions could be added, for instance that each link has to be connected to four springs. Furthermore, a distribution of values of l_0 and, therefore, k could be applied in this case, making it very complex but a more realistic model. This sophisticated system would be computationally challenging, and it is left to future investigations, that will help to tackle unanswered questions.

However, it may be pointed out that this would be a great starting point to study the entropy of polymer networks. Effects such as the mentioned eCe could be investigated then. Calculations of the entropy of the system would need to be performed in the computational program. In the initial simplified case, only the entropy S_{chain} corresponding to the shape of a chain section is taken into account. S_{chain} concerns the number of micro-states of a single chain given its length and end-to-end distance. However, in a real system there is also the contribution of the entropy related to the geometric distribution of the cross-links S_{nodes} (e.g. different ways of distributing a given number of nodes in space). To make a correct treatment of the entropy both terms would need to be considered.

III. CONCLUSIONS

A model to describe basic components of polymer networks that compose elastomers has been presented. The model consists of an ensemble of non-interacting springs fixed at one spring-end and subjected to an external force. An analytical expression for the partition function and the expected values of the considered system has been provided. This has been combined with MC simulations allowing to investigate numerically the dependence of the thermodynamic magnitudes on temperature and applied force. An agreement between the calculated expressions and the numerical results has been confirmed.

The flattening of the system in the transverse direction when applying a force has been successfully modelled. However, a variation (i.e. no conservation) of the estimated volume has been found. The lack of a geometric factor in the model that accounts for a realistic distribution of polymer chains has been proposed as a possible explanation for the non-conservation of volume. The phenomenon of contraction in the direction of the applied force when the force is constant and temperature raises has been correctly verified. Finally, a well behaved evolution of crystallization in the process of stretching has been shown thanks to MC simulations.

Since the model is a non-interacting simplification, future steps to develop a more realistic model have been discussed at the end, which could be implemented in the written MC code. The resulting model will hopefully allow to improve the fundamental understanding of some of the properties of elastomers, such as the hysteresis cycle for the strain-stress curves or crystallization, which are important features to improve the efficiency and sustainability of cooling machines based on caloric effects.

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IV. APPENDIX

The integrals that appear in the expressions of the expected values in section II A are:

$$I_{s1} = \int_0^{\infty} l \exp^{-\beta H_L} \sinh(\beta Fl) dl, \quad (9)$$

$$I_{c2} = \int_0^{\infty} l^2 \exp^{-\beta H_L} \cosh(\beta Fl) dl, \quad (10)$$

$$I_{s3} = \int_0^{\infty} l^3 \exp^{-\beta H_L} \sinh(\beta Fl) dl. \quad (11)$$

H_L is given by Eq 2. This notation has been chosen in order to write compact expressions for the expected values. The first sub-index “s/c” corresponds to the trigonometric function that appears in the integral ($\sinh(\beta Fl)$ or $\cosh(\beta Fl)$), whereas the second sub-index (e.g., the number) corresponds to the power of l in the integral.

To determine these integrals, first they are broken into two ranges of integration (from 0 to l_0 and from l_0 to ∞). Since $H_L = 0$ for $l < l_0$, the exponential of the first term simplifies. The second is calculated by writing the

hyperbolic function in terms of the exponential function (using its definition). An example for I_{s1} is developed below:

$$I_{s1} = \int_0^{l_0} l \sinh(\beta Fl) dl + \int_{l_0}^{\infty} l e^{-\beta \frac{1}{2}(l-l_0)^2} \frac{e^{\beta Fl} - e^{-\beta Fl}}{2} dl.$$

Finally, three integrals need to be calculated because:

$$I_{s1} = \int_0^{l_0} l \sinh(\beta Fl) dl + \frac{1}{2} \int_{l_0}^{\infty} l e^{-\beta \frac{1}{2}(l-l_0)^2 + \beta Fl} dl - \frac{1}{2} \int_{l_0}^{\infty} l e^{-\beta \frac{1}{2}(l-l_0)^2 - \beta Fl} dl.$$