Elastocaloric effect in liquid crystal elastomers from molecular simulations

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ABSTRACT

Large-scale molecular simulations of the elastocaloric effect in swollen monodomain main-chain liquid crystal elastomers are performed, following the so-called indirect approach where the magnitude of the effect is extracted from the system's equation of state connecting stress, strain, and temperature. The presented isostress off-lattice Monte Carlo simulations are based on the soft-core Gay-Berne potential and predict an elastocaloric temperature increase that exceeds ~ 10 K upon applying an external engineering stress of 100 kPa, which results in an elastocaloric responsivity beyond ~ 100 K/MPa.

KEYWORDS

Elastocaloric effect; liquid crystal elastomer; Monte Carlo simulation; Gay-Berne potential

1. Introduction

Elastocaloric (eC) effects are reversible thermal changes observed in elastic materials submitted to an external stretching or compression mechanical field. Together with other caloric effects (electro- and magnetocaloric) they have attracted significant attention because of their potential use in novel cooling devices and heat pumps [1–3]. Materials featuring eC effects include shape-memory alloys [1,3], fast-ion conductors [4], carbon nanotubes, and graphene [5]. The rather large mechanical fields required in these systems to achieve notable thermal effects may be avoided by using soft materials such as liquid crystal elastomers (LCE) [6,7]. LCE consist of weakly crosslinked polymer networks with embedded liquid-crystalline (mesogenic) units and feature a very pronounced coupling between the strain of the polymer network and the orientational order of embedded mesogens. The latter also provide a structural (orientational) nematic-isotropic (NI) transition where the eC response is expected to be largest.

Experimentally, a measurable eC response has already been observed in main-chain LCE [8], but at a fraction of the stress field required in other eC materials, e.g., in NiTi-based shape-memory alloys [3,9–11]. The amplitude of the observed eC effect was of the order of 0.1 K and the corresponding responsivity in the range of a few K/MPa. In the present study, we would like to readdress the issue through molecular simulation,

performing large-scale Monte Carlo (MC) simulations of swollen monodomain main-chain LCE to estimate the amplitude of the eC effect, as well as the corresponding responsivity.

2. Thermodynamic background

There are two possible approaches to obtain the amplitude ΔT of the eC effect [1]. In the so-called direct approach, ΔT is measured under adiabatic application or removal of external force $\mathcal{F}$ like in Ref. [8]. On the other hand, the indirect approach that we follow here starts by considering the total entropy of the sample, S , as a function of temperature T and external force $\mathcal{F}$, and setting $S = \text{const.}$ for a reversible adiabatic process. In a LCE sample, an external stretching force enhances the orientational ordering of the elongated mesogenic units through the strain-alignment coupling, thereby decreasing the corresponding entropy contribution. Given the adiabatic conditions, the ‘thermal’ entropy contribution must increase accordingly, which manifests itself in an increase of sample temperature. The constant-entropy constraint $dS = (\partial S/\partial T)_{\mathcal{F}}dT + (\partial S/\partial \mathcal{F})_Td\mathcal{F} = 0$ implies that the infinitesimal adiabatic changes of temperature and stretching force dT and $d\mathcal{F}$ are related by

$$\frac{dT}{d\mathcal{F}} = -\frac{\left(\frac{\partial S}{\partial \mathcal{F}}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_{\mathcal{F}}} = -\frac{T}{C_{\mathcal{F}}} \left(\frac{\partial \ell}{\partial T}\right)_{\mathcal{F}}, \quad (1)$$

where the sample heat capacity at constant force, $C_{\mathcal{F}} = T(\partial S/\partial T)_{\mathcal{F}}$, has been introduced [12], and ℓ denotes the length of the sample. Above, the temperature derivative of ℓ originates from a suitable Maxwell relation [12], $(\partial S/\partial \mathcal{F})_T = (\partial \ell/\partial T)_{\mathcal{F}}$, and can be calculated from the equation of state $\ell(T, \mathcal{F})$, if known, or deduced from either experimental or simulation data. In the following we perform isostress Monte Carlo simulations to obtain both $\ell(T, \mathcal{F})$ and $C_{\mathcal{F}}(T, \mathcal{F})$, and integrate Eq. (1) to estimate the amplitude of the eC effect, ΔT . A similar approach has been used in Ref. [13] to calculate the amplitude of the electrocaloric effect from microscopic simulations.

3. Molecular model and simulations

We consider main-chain (rather than side-chain) LCE because of their extreme strain-alignment coupling [6] leading to large values of $(\partial \ell/\partial T)_{\mathcal{F}}$ and, presumably, a large elastocaloric ΔT . The simulations are based on the soft-core Gay-Berne (GB) potential [14,15] favouring parallel alignment of elongated particles. Uniaxial soft-core GB ellipsoids are used here to assemble LCE networks, representing bonded mesogenic molecules, as well as the non-bonded mesogenic swelling monomers. For compatibility with previous work [16,17], the ratio of potential well depths for a pair of aligned GB particles in the end-to-end and side-to-side relative positions is fixed at 0.2, and the length-to-width ratio of all GB ellipsoids is taken to be equal to 3. Bonding sites are assumed at the GB particle ends (head/tail) as well as on the equator wherever needed to provide cross-links creating a LCE network. The interparticle bonds are modelled by means of the finitely extensible nonlinear elastic (FENE) [18] potential applied to both bond stretching and bending. The maximum bond length is set to ~ 0.4 molecular widths. The polymer chains are assumed to be rather flexible, with a persistence length approaching ~ 2 molecular lengths for isolated chains. The easy

Figure 1. A sequence of LCE sample snapshots upon applying external stress at $T^* = 5.75$; stress values are given in terms of reduced engineering stress σ^* and displayed next to each snapshot. Orientations of the bonded ellipsoids are colour-coded; red, green, and blue correspond to an alignment along x , y , and z -axes, respectively; swelling monomers are shown in grey. External stress is applied along the z -axis. *Top left:* Schematic depiction of LCE network architecture (taken from Ref. [16]).

Figure 2. *Bottom:* Temperature dependence of the reduced sample dimension λ_z for different values of applied stress: $\sigma^* = 0$ (+), 0.02 ($\times$), 0.04 ($\square$), 0.06 ($\circ$), 0.08 ($\triangle$), and 0.1 ($\diamond$). *Top:* The corresponding specific heat $c_{\mathcal{F}}^*$ dependences, given per particle and in units of k_B .

Figure 3. Selected adiabatic curves (thick white lines) as obtained by integrating Eq. (2) across the temperature—stress plane. The contour plot depicts the magnitude of the interpolated adiabatic derivative $dT^*/d\sigma^*$; large values of the derivative (light colour shades) are observed close to the NI transition at low stress and result in a more significant adiabatic temperature variation per unit applied stress.

bond orientation is taken parallel to the long molecular axis for the head/tail sites, and along the short molecular axis for the equatorial site. Further details regarding the potential parameters are given in Ref. [16] and in references therein.

The elastomer network is generated using the ‘isotropic genesis’ procedure [16] in a cubic simulation box with periodic boundary conditions. First, polydisperse (on average ~ 8 GB units long) polymer chains are grown at low density in random directions, each starting from a random position within the simulation box. Then, the active chain heads/tails are connected laterally to the equatorial sites on the nearest neighbouring chains. The network structure obtained in this way is depicted schematically in Fig. (1). After crosslinking, additional swelling monomers are introduced, like in some experimental samples [19], but also to facilitate MC equilibration through an increased mobility of polymer chains. Finally, the sample is compressed almost to close-packing, yielding a so-called ‘reference’ sample. In total, the sample consists of $N = 64000$ particles; out of these, 33024 are swelling monomers. The crosslink fraction is close to $\sim 12\%$ [16].

Equilibrium sample configurations are now obtained from iso-stress MC simulations, following a modified Metropolis algorithm where both temperature and external stress are fixed [20], while the cubic simulation box constraint is lifted. The MC trial moves include individual GB particle moves (separate translation and rotation), bonded particle pair rotations (excluding crosslinks), and collective sample resize moves carried out at constant volume, keeping the cuboidal simulation box shape [16]. More than 16×10^6 MC cycles are performed for equilibration, and further $\sim 10^6$ cycles for production. (One MC cycle consists of attempting to move/rotate each of the particles and all eligible particle pairs.) The resize moves are carried out every 5 cycles. All move amplitudes are adjusted on-the-fly to maintain an acceptance ratio close to 50%. Verlet neighbour lists with a suitable cutoff (5 molecular widths) and cell-linked lists are used to reduce the computational effort [21], and parallelisation is employed to speed up calculations.

The eC effect will be most pronounced in monodomain LCE samples where, in the

Figure 4. Temperature dependence of elastocaloric effect amplitude ΔT^* for different values of applied stress: $\sigma^* = 0.02$ (a), 0.04 (b), 0.06 (c), 0.08 (d), and 0.1 (e).

aligned nematic phase, the director is uniform throughout the sample. Note that the isotropic-genesis procedure used to generate our sample has actually been developed for the creation of polydomain systems lacking global alignment. However, in a relatively small system like ours, the parallel aligning tendency of the GB ellipsoids can overcome polymer network irregularities, yielding a (nearly) monodomain sample after a long MC equilibration at zero stress deep in the nematic phase [16]. At the end of this equilibration, large stress is applied along the axis of alignment to stretch the sample and to enhance its monodomain character, and then removed. The resulting sample is then first equilibrated in a zero-stress run separately at each temperature, and then used as a starting configuration in the subsequent runs at nonzero external stress.

4. Results and discussion

Fig. 2, *bottom*, shows the average sample length λ_z along the direction of applied stress, z -axis, as a function of temperature T^* and external engineering stress σ^* , while the corresponding selected molecular snapshots are shown in Fig. 1. The reduced quantities used in Fig. 2 are defined as follows: λ_z is the simulation box size measured along the z -axis, normalised with respect to a side of the reference cubic sample. The reduced temperature is given by $T^* = k_B T / \epsilon$, where ϵ is a characteristic interaction energy (i.e., the depth of the GB potential well for the parallel side-to-side molecular alignment) and k_B the Boltzmann constant. Further, reduced stress is introduced as $\sigma^* = \Sigma \sigma_0^3 / \epsilon$, where Σ stands for engineering stress (calculated with respect to the surface area corresponding to a face of the cubic reference sample) and σ_0 is the GB particle width. The simulated data presented in Fig. 2, *bottom*, substitute the equation of state $\ell(T, \mathcal{F})$ and are used to calculate the temperature derivatives needed in the ‘indirect’ analysis of the eC response.

The zero-stress curve in Fig. 2, *bottom*, shows a NI transition at $T_{NI}^* \sim 5.75$. As discussed in Refs. [17,22], the order parameter dependence (and, consequently, the λ_z dependence) across the NI transition in LCE can be rather smooth. In the vicinity of the transition, the absolute value of the derivative $(\partial \ell / \partial T)_{\mathcal{F}}$ appearing in the numerator of Eq. (1) is rather high. The temperature-scan curves for $\sigma^* \neq 0$ are even smoother, with the highest slopes at a T^* somewhat above the NI transition. At the

Figure 5. Elastocaloric responsivity as a function of applied stress in an experiment with initial temperature $T^* = 5.5$, just below the NI transition.

same time, Fig. 2, *top*, shows the corresponding behaviour of the reduced specific heat $c_{\mathcal{F}}^*$ at constant force/stress, defined as $C_{\mathcal{F}}/Nk_B$. In our simulation, $c_{\mathcal{F}}^*$ is calculated as the temperature derivative of average enthalpy $\langle U \rangle - \mathcal{F}\langle \ell \rangle$ at constant force [12], where U stands for the total (kinetic plus interaction) internal energy. Here for elongated rigid GB particles with 5 kinetic degrees of freedom (3 translational and 2 rotational) an average kinetic energy contribution of $(5/2)k_B T$ per particle has been assumed, while the interaction part of U is obtained directly from simulation. Note that $c_{\mathcal{F}}^*$ appearing in the denominator of Eq. (1) also peaks close to the NI transition; the total value of the elastocaloric derivative $dT/d\mathcal{F}$, however, still peaks close to T_{NI}^* (see Fig. 3).

To estimate the amplitude of the eC effect, Eq. (1) has to be properly integrated. In terms of reduced quantities introduced above it can be rewritten as

$$\frac{dT^*}{d\sigma^*} = -\frac{T^*}{\rho^* c_{\mathcal{F}}^*} \left(\frac{\partial \lambda_z}{\partial T^*} \right)_{\sigma^*}, \quad (2)$$

where $\rho^* = N\sigma_0^3/V \sim 0.287$ denotes the reduced sample density, V being the sample volume. The expression on the r.h.s. of Eq. (2) is a function of both T^* and σ^* , therefore small increments of σ^* should be considered when iteratively calculating the temperature change. Since only a modest number of data points are currently available from our simulation, first-order interpolation of $\lambda_z(T^*, \sigma^*)$ and $c_{\mathcal{F}}^*(T^*, \sigma^*)$ is used to provide the necessary intermediate values. Note, however, that these steps are justified only if both λ_z and $c_{\mathcal{F}}^*$ are well-behaved functions, which, in general, may not necessarily be the case close to a phase transition.

Temperatures on the abscissa in Fig. (4) correspond to the initial temperatures of the simulated adiabatic experiment. Therefore, the highest eC amplitude ΔT^* is observed for initial temperatures just below T_{NI}^* (note that the temperature upon applying stress notably increases). In addition, a secondary peak appears in the ΔT^* dependence slightly above $T^* \sim 6.5$. It can be attributed to a non-vanishing value of the $(d\ell/dT)_{\mathcal{F}}$ derivative in this T^* and σ^* range, accompanied by a rather low value of heat capacity $C_{\mathcal{F}}$ far from the NI transition; see also the contour plot in Fig. 3. Note, however, that in experiments [8] such a secondary peak has not been observed. Its presence in the simulation may be a mere consequence of local irregularities in our relatively small sample. This suggests that the predicted eC response, given in Fig. (4)

and below, should be interpreted carefully and regarded as an estimate.

Applying an external stress $\sigma^* = 0.1$ — the largest stress value considered — an eC amplitude of $\Delta T^* \sim 0.24$ is observed. Taking $\epsilon = 9.3 \times 10^{-22}$ J and $\sigma_0 = 1$ nm like in Ref. [16] (yielding a NI transition at approximately 390 K), this corresponds to an elastocaloric ΔT well above 10 K when an engineering stress of ~ 100 kPa is applied. The resulting eC responsivity, Fig. (5), then reaches values that exceed 100 K/MPa. Comparing with the experimental results presented in Ref. [8], current simulations predict an enhancement of the eC response in LCE by more than one order of magnitude both in its amplitude and responsivity. At the same time, other existing (non-soft) eC materials are capable of exhibiting adiabatic temperature changes comparable to those seen in our simulation, but the corresponding eC responsivities appear to be 2-3 orders of magnitude lower due to the significantly larger stresses applied [1].

As already mentioned, the eC amplitude observed in simulation should be interpreted with care. The simulated value of the $(\partial\lambda_z/\partial T)_{\mathcal{F}}$ derivative just below the NI transition at zero stress is estimated as $\sim 0.04/\text{K}$, which is higher than in current experiments [23]. This suggests that the existing experimental samples still show potential for further optimisation. However, considering separately the simulated sample specific heat, $c_{\mathcal{F}} = c_{\mathcal{F}}^* k_B N_A / M$, where N_A and M are the Avogadro number and the monomer kilomolar mass, respectively, and putting $c_{\mathcal{F}}^* \approx 6$ (see Fig. 2, top) and $M \approx 250$ kg/kmol (as, e.g., for the 5CB liquid crystal [24]), yields $c_{\mathcal{F}} \approx 200$ J/kgK. Experiments, on the other hand, give values around 2000 J/kgK, which indicates that our simulation based on structureless GB particles (lacking, e.g., internal molecular degrees of freedom) underestimates the specific heat and, consequently, is likely to overestimate the overall eC amplitude.

All in all, the above prediction of eC performance should be regarded as a preliminary simulation trial that can be subject to further improvement. On the sample preparation side, like in the real experiment, the relevant structural and physical features to be optimised include the elastomer network architecture (crosslinker density and the degree of anisotropy imprinted mechanically upon synthesis), mesogenic unit properties (nematic-isotropic transition temperature), and the degree of sample swelling. In addition, the entire study could be improved by considering several sample replicas or, alternatively, a single but significantly larger and hence more representative sample.

5. Conclusions

We have performed large-scale molecular simulations of the elastocaloric effect in swollen main-chain liquid crystal elastomers. The estimates for the elastocaloric response are obtained via the so-called ‘indirect’ route from the simulated equation of state. Our isostress Monte Carlo simulations performed in a system of soft Gay-Berne ellipsoids predict a temperature increase of more than 10 K when an external stress of 100 kPa is applied, and, consequently, an elastocaloric responsivity of more than 100 K/MPa. Even without specific optimisations of the simulated system, both values exceed the current experimental benchmarks by more than one order of magnitude but may be somewhat overestimated due to the disagreement of the simulated and experimental specific heat values. Nevertheless, liquid crystal elastomers as elastocaloric materials appear to show considerable potential for further improvement and use in applications.

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Disclosure statement

There is no potential conflict of interest to be declared.

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References

- [1] Moya X, Kar-Narayan S, Mathur ND, Caloric materials near ferroic phase transitions. *Nat. Mater.* 2014;13:439–450.
- [2] Crossley S, Mathur ND, Moya X, New developments in caloric materials for cooling applications. *AIP Adv.* 2015;5:067153.
- [3] Tušek Jaka, Engelbrecht K, Eriksen D, Dall’Olio S, Tušek Janez, Pryds N, A regenerative elastocaloric heat pump. *Nat. Energy* 2016;1:16134.
- [4] Sagotra AK, Errandonea D, Cazorla C, Mechanocaloric effects in superionic thin films from atomistic simulations. *Nat. Commun.* 2017;8:963.
- [5] Lisenkov S, Herchig R, Patel S, Vaish R, Cuzzo J, Ponomareva I, Elastocaloric effect in carbon nanotubes and graphene, *Nano Lett.* 2016;16:7008–7012.
- [6] Warner M, Terentjev EM, *Liquid Crystal Elastomers*. Oxford (UK): Oxford University Press; 2007.
- [7] Küpfer J, Finkelmann H, Nematic liquid single crystal elastomers. *Macromol. Chem. Rapid Commun.* 1991;12:717–726.
- [8] Trček M, Lavrič M, Cordoyiannis G, Zalar B, Rožič B, Kralj S, Tzitzios V, Nounesis G, Kutnjak Z, Electrocaloric and elastocaloric effects in soft materials. *Philos. Transact. A Math. Phys. Eng. Sci.* 2016;374:20150301.
- [9] Cui J, Wu YM, Muehlbauer J, Hwang YH, Radermacher R, Fackler S, Wuttig M, Takeuchi I, Demonstration of high efficiency elastocaloric cooling with large ΔT using NiTi wires. *Appl. Phys. Lett.* 2012;101:073904.
- [10] Pieczyska EA, Gadaj SP, Nowacki WK, Tobushi H, Phase-transformation fronts evolution for stress- and strain-controlled tension tests in TiNi shape memory alloy, *Exp. Mech.* 2006;46:531–542.
- [11] Shaw AJ, Kyriakides S, Thermo-mechanical aspects of NiTi, *J. Mech. Phys. Solids* 1995;43:1243–1281.
- [12] Callen HB, *Thermodynamics and an introduction to thermostatistics*. New York (NY): John Wiley & Sons; 1985.
- [13] Ponomareva I, Lisenkov S, Bridging the macroscopic and atomistic descriptions of the electrocaloric effect. *Phys. Rev. Lett.* 2012;108:167604.
- [14] Berardi R, Zannoni C, Lintuvuori JS, Wilson MR, A soft-core Gay-Berne model for the simulation of liquid crystals by Hamiltonian replica exchange. *J. Chem. Phys.* 2009;131:174107–174112.

- [15] Gay JG, Berne BJ, Modification of the overlap potential to mimic a linear site-site potential. *J Chem Phys* 1981;74:3316–3319.
- [16] Skačej G, Zannoni C, Molecular simulations shed light on supersoft elasticity in polydomain liquid crystal elastomers. *Macromolecules* 2014;47:8824–8832.
- [17] Skačej G, Sample preparation affects the nematic-isotropic transition in liquid crystal elastomers: insights from molecular simulation. *Soft Matter* 2018;14:1408-1416.
- [18] Bird RB, Armstrong RC, Hassager D, Dynamics of polymeric liquids. New York (NY): Wiley; 1971.
- [19] Urayama K, Honda S, Takigawa T, Electrooptical effects with anisotropic deformation in nematic gels. *Macromolecules* 2005;38:3574–3576.
- [20] Frenkel D, Smit B, Understanding molecular simulation: From algorithms to applications. San Diego (CA): Academic Press; 2002.
- [21] Allen MP, Tildesley DJ, Computer simulation of liquids. Oxford (UK): Clarendon Press; 1991.
- [22] Selinger JV, Jeon HG, Ratna BR, Isotropic-nematic transition in liquid-crystalline elastomers, *Phys. Rev. Lett.* 2002; 89:225701.
- [23] Rožić B, Kutnjak Z, private communication.
- [24] Collings PJ, Hird M, Introduction to liquid crystals: Chemistry and physics. London (UK): Taylor and Francis; 2009.