



Unusual Mechanocaloric Property of Rubber

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Recent precise measurement of the mechanocaloric properties of rubber exhibits non-monotone dependence of the temperature on tension when it is applied adiabatically. The unusual mechanocaloric effect is explained on the basis of a modified folding ruler model in which an attractive interaction exists between adjacent folded units. It is shown that the non-monotone behavior is caused by competition between energetic and entropic effects of the rubber.

An adiabatic stretch of rubber is known to raise its temperature. The physics behind this mechanocaloric effect has been understood by the entropy of rubber. The entropy of rubber is large when the rubber is at rest and becomes small when it is stretched. Therefore, when a stretching force is applied adiabatically, the temperature increases to compensate the loss of entropy due to stretching. The simplest model to explain this physics is the folding ruler model where the ruler is placed in one dimension and each unit of the ruler can point either plus or minus direction freely.¹⁾

Recently, Matsuo et al. devised a new apparatus for precise measurement of mechanocaloric properties of rubber, and reported that, when the applied force is increased adiabatically from zero, the temperature of rubber decreases initially before it increases.²⁾

In this letter, I present a modified folding ruler model which explains the unusual mechanocaloric effect of rubber. The model consists of N identical units which are connected to its neighbors at their end points and placed on one dimensional space as shown in Fig. 1. Each unit can point either plus or minus direction. The left side of the first unit is fixed at the origin and the length of the system is given by the position of the right side of the N -th unit. The model can be mapped onto the Ising model. To this end, I assign spin variable S_i to the i -th unit, where $S_i = +1$ and -1 denote the plus and minus directions, respectively. The length L of the model rubber is given by

$$L = \ell \sum_{i=1}^N S_i, \quad (1)$$

where ℓ is the length of a unit. I assume that a joint between folded pair of units has an energy ε and the energy of a joint connecting stretched pair of units is zero. Therefore, the energy of the model rubber is given by

$$E = \frac{\varepsilon}{2} \sum_i (1 - S_i S_{i+1}), \quad (2)$$

where I ignored the boundary effect. When a tension X is applied at both ends, the T-P partition function $Y(T, X, N)$ is given by¹⁾

$$Y(T, X, N) = \sum_{\{S_i = \pm 1\}} \exp \left[-\frac{\varepsilon}{2k_B T} \sum_i (1 - S_i S_{i+1}) + \frac{X\ell}{k_B T} \sum_{i=1}^N S_i \right], \quad (3)$$

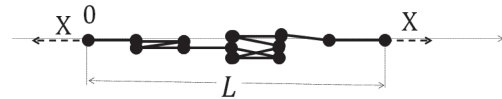


Fig. 1. The folding ruler model of rubber.

where T is the temperature and k_B is the Boltzmann constant. The expression for the partition function is essentially equivalent to the canonical partition function for the Ising model under an external field and the partition function can readily be calculated by the transfer matrix formalism.³⁾ The Gibbs free energy $G(T, X, N)$ is given by $G(T, X, N) = -k_B T \ln Y(T, X, N)$ which is written, in the thermodynamic limit, as

$$G(T, X, N) = \frac{N\varepsilon}{2} - Nk_B T \ln y(T, X, \varepsilon), \quad (4)$$

where

$$y(T, X, \varepsilon) = \cosh \frac{X\ell}{k_B T} + h(T, X, \varepsilon),$$

$$h(T, X, \varepsilon) = \sqrt{\sinh^2 \frac{X\ell}{k_B T} + e^{-\frac{2\varepsilon}{k_B T}}}.$$

The average length $\langle L \rangle = -(\frac{\partial G}{\partial X})_{T, N}$ and the entropy $S = -(\frac{\partial G}{\partial T})_{X, N}$ are then given by

$$\frac{\langle L \rangle}{N\ell} = \frac{\sinh \frac{X\ell}{k_B T}}{h(T, X, \varepsilon)}, \quad (5)$$

$$\frac{S}{Nk_B} = \ln y(T, X, \varepsilon)$$

$$+ \frac{1}{h(T, X, \varepsilon)} \left[\frac{1}{y(T, X, \varepsilon)} \frac{\varepsilon}{k_B T} e^{-\frac{2\varepsilon}{k_B T}} - \frac{X\ell}{k_B T} \sinh \frac{X\ell}{k_B T} \right]. \quad (6)$$

It is easy to confirm that these expressions (4)–(6) reduce to the well-known results when $\varepsilon = 0$.

In the following discussion, I focus on the case of $\varepsilon < 0$, which denotes that a folded pair is favorable compared to a stretched pair, since the case of $\varepsilon > 0$ shows similar behavior to the system of no interaction $\varepsilon = 0$. Equation (5) represents the equation of state which is shown in Fig. 2 for $\varepsilon/X_0\ell = -1$. Here, X_0 is a scale of tension and thus the energy is scaled by $X_0\ell$. Figure 3 shows the temperature dependence of the average length of the model rubber for $X/X_0 = 0.5, 1, 2$ when $\varepsilon/X_0\ell = -1$. For small tension, the average length shows a maximum as a function of temperature.

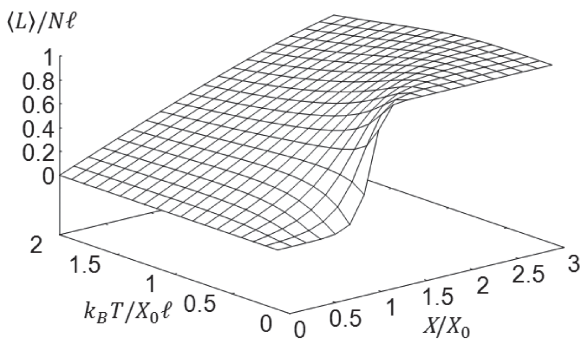


Fig. 2. The equation of state of the model rubber when $\varepsilon/X_0\ell = -1$.

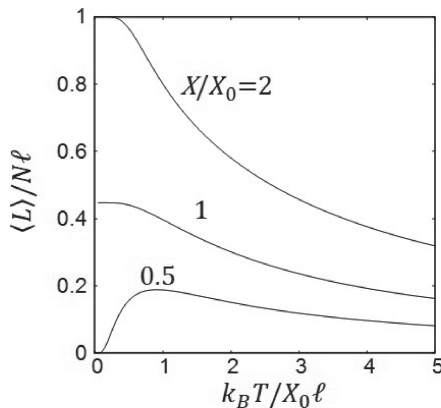


Fig. 3. The temperature dependence of the length of the model rubber for fixed tension $X/X_0 = 0.5, 1, 2$ when $\varepsilon/X_0\ell = -1$.

Figure 4 shows the temperature dependence of the entropy of the model rubber for $X/X_0 = 0, 0.5, 1, 2$ when $\varepsilon/X_0\ell = -1$, and Fig. 5 shows the tension dependence of the entropy of the model rubber for $k_B T / X_0 \ell = 0.2, 0.5, 1, 2$ when $\varepsilon/X_0\ell = -1$.

Since the entropy change is given by

$$dS = \left(\frac{\partial S}{\partial X}\right)_T dX + \left(\frac{\partial S}{\partial T}\right)_X dT \quad (7)$$

the tension dependence of temperature for the adiabatic process where $dS = 0$ is determined by $(\frac{\partial S}{\partial X})_T$ and $(\frac{\partial S}{\partial T})_X$. Therefore, Figs. 4 and 5 indicate that the temperature for small tension can be a non-monotone function. In fact, the tension dependence of the temperature for the adiabatic process can be obtained from Eq. (6). Figure 6 shows the tension dependence of the temperature of the model rubber for the adiabatic stretch at $\frac{S}{Nk_B} = 0.3, 0.5$ when $\frac{\varepsilon}{X_0\ell} = -1$.

Now, using the present model, I analyze the experimental data provided by Matsuo.⁴⁾ Since the energy in Eq. (3) refers to a single polymer chain, the external force must be that acting on a single chain. Therefore, if the force X in Eq. (3) is the force acting on rubber, then it must be replaced by X/M , where the rubber is assumed to consist of M independent polymer chains. Since the present model is extremely simple, it is not obvious to relate parameters of the model, $\varepsilon, S_0, X_0, \ell, M$ to properties of the rubber, and thus I took $M\varepsilon/X_0\ell, S_0/Nk_B, X_0, X_0\ell/Mk_B$ as fitting parameters. Figure 7 shows experimental data for the force dependence of temperature in the adiabatic extension of rubber by solid circles⁴⁾ and the fitting of the data on the basis of the present model by the solid curve. Here, parameters are set as follows:

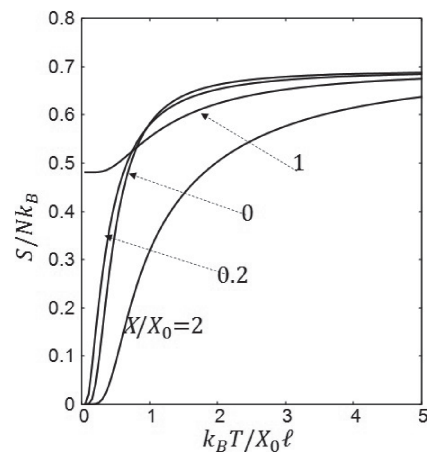


Fig. 4. The temperature dependence of the entropy of the model rubber for fixed tension $X/X_0 = 0, 0.5, 1, 2$ when $\varepsilon/X_0\ell = -1$.

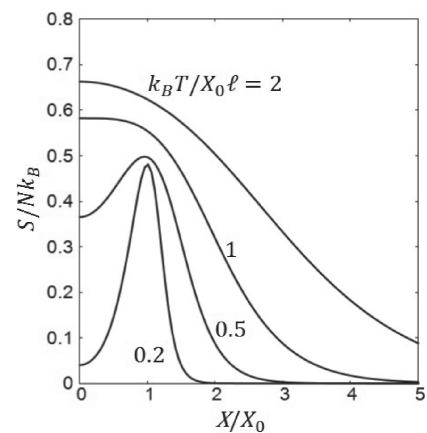


Fig. 5. The tension dependence of the entropy of the model rubber for fixed temperature $k_B T / X_0 \ell = 0.2, 0.5, 1, 2$ when $\varepsilon/X_0\ell = -1$.

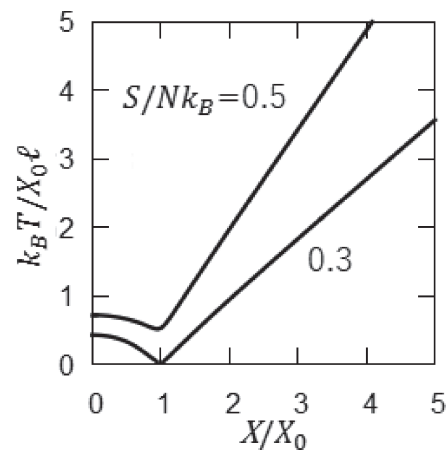


Fig. 6. The tension dependence of the temperature of the model rubber for the adiabatic processes at $S/Nk_B = 0.3, 0.5$ when $\varepsilon/X_0\ell = -1$.

$$M\varepsilon/X_0\ell = -0.08, \quad S_0/Nk_B = 0.58195, \\ X_0\ell/Mk_B = 3750.4394 \text{ [K]}, \quad X_0 = 400.9523 \text{ [N]}, \quad (8)$$

which were determined to get good fitting around the minimum of the curve. It should be mentioned to that the result is very much sensitive to the value of parameters and

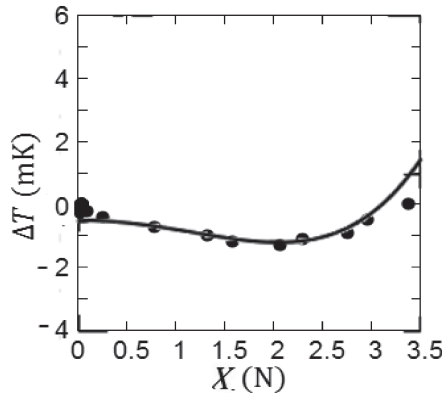


Fig. 7. Fitting of the force dependence of the temperature in the adiabatic extension of rubber by the present model. Solid circles are experimental data provided by Matsuo⁴⁾ and the solid curve is the theoretical prediction by Eq. (6), where $\Delta T = T - 299.65$ and parameters are set as in Eq. (8).

the numbers in Eq. (8) is a set of values which reproduced a good fitting. It should also be noted that the temperature change ΔT observed in experiments⁴⁾ is in the order of mK at the room temperature $T_0 \sim 300$ K and one needs relative accuracy at least in the order of $\Delta T/T_0 \sim 10^{-6}$ to fit the date. It can easily be confirmed that these values are consistent to material parameters.

The position of the minimum of the curve shown in Fig. 7 is determined by $(\partial S/\partial X)_T = 0$, or equivalently by $(\partial \langle L \rangle / \partial T)_X = 0$ due to the Maxwell relation, and thus it is given by

$$\varepsilon = -X\ell \coth \frac{X\ell}{k_B T}. \quad (9)$$

The behavior of the temperature near $X = 0$ can readily be analyzed. Near $X = 0$, the entropy is written as

$$\frac{S(T)}{Nk_B} = \ln \left(2 \cosh \frac{\varepsilon}{2k_B T} \right) - \frac{\varepsilon}{2k_B T} \tanh \frac{\varepsilon}{2k_B T} - \frac{1}{2} \left(\frac{X\ell}{k_B T} \right)^2 \left(1 + \frac{\varepsilon}{k_B T} \right) e^{\frac{\varepsilon}{k_B T}}. \quad (10)$$

Therefore, for the adiabatic process where the entropy is kept at $S(T) = S_0$,

$$\begin{aligned} & -\frac{1}{2} \left(\frac{X\ell}{k_B T} \right)^2 \left(1 + \frac{\varepsilon}{k_B T} \right) e^{\frac{\varepsilon}{k_B T}} \\ &= \frac{S_0}{Nk_B} - \ln \left(2 \cosh \frac{\varepsilon}{2k_B T} \right) - \frac{\varepsilon}{2k_B T} \tanh \frac{\varepsilon}{2k_B T} \\ &\equiv G(T). \end{aligned} \quad (11)$$

Setting $T(X = 0) = T_0$ and expanding the right hand side $G(T)$ around $T = T_0$, I find that $G(T_0) = 0$ and $G(T)$ can be expanded as

$$G(T) \sim G'(T_0)(T - T_0). \quad (12)$$

Therefore, the behavior of the temperature near $X = 0$ is expressed as

$$T - T_0 \sim -\frac{1}{2G'(T_0)} \left(\frac{X\ell}{k_B T_0} \right)^2 \left(1 + \frac{\varepsilon}{k_B T_0} \right) e^{\frac{\varepsilon}{k_B T_0}}. \quad (13)$$

It can be shown that the coefficient on the right-hand side is negative, indicating that the T vs X curve is convex upward at $X = 0$.

Exploiting a modified folding ruler model of rubber, I showed that the unusual mechanocaloric properties of rubber can be explained by an interaction due to chemical bonding that favors the folded structure between adjacent polymer units. I also showed that the present simple model can reproduce the experimental data as shown in Fig. 7. When the tension is weak, the energetic effect is dominant and the increased tension under an adiabatic condition reduces the temperature and when the tension is increased further, the entropic effect takes over and the temperature rises when the tension is increased.

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