臺灣二ＯＯ八年國際科學展覽會

科　　　別：物理與太空科學

作 品 名 稱：橡膠鍵鏈結構與自由能的關係

得 獎 獎 項：第二名
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作者介紹

從小生長在山環水繞，步調悠閒的小城鎮，因而有更多觀察大自然的機會。雖論不上張目對日，但明察秋毫是我一直以來的生活樂趣。這次的研究，可以算是我人生中的第一個實驗，由於家人給予包容和支持，讓實驗能夠成為我不可或缺的精神食糧，更在教授、學長、學姊和老師的引領之下，幫助我學習到更深入思考與分析的能力，接近物理這座美麗的殿堂。

摘要

受應力拉伸時，橡膠溫度明顯上升；縮放回原長，橡膠溫度驟降。由文獻得知橡膠內部具有特殊的鍵鍊結構，在一般的情況下，交鏈分子糾結成一團，狀態複雜；受外力拉伸時，交鏈分子依橡膠長度之增加而伸展，排列較爲整齊，狀態之複雜度減小。

根據熱力學第一定律，當內能變化爲零，則外力作功會造成能量變化。在定溫之下，橡膠內能變化爲零，當其受應力拉伸，使其內部交鏈分子排列複雜度降低，造成橡膠熵值減小，而有能量（dQ=TdS）的釋出。測量此一能量 dQ 變化，即可計算出熵與狀態數之變化

Abstract

The temperature of rubber rises as it is stretched, its temperature comes back again while it restores to its original length. It is known that the rubber is consisted of long-chain molecules, the long-chain molecules strangle each other at normal state, however, they become more order when the rubber is stretched. Based on the 1st law of thermodynamics $dU=dQ+dW$, The deformation caused by applied force supplies energy to the rubber and reduce its entropy, the heat dQ (=TΔS) released by the reduction of entropy causes the temperature rise of rubber as dU=0. We report the study on the correlation of thermal properties and the molecular network in rubber, from the measurements of temperature change, the changes of entropy and the changes of states' number were estimated.

壹、 研究動機

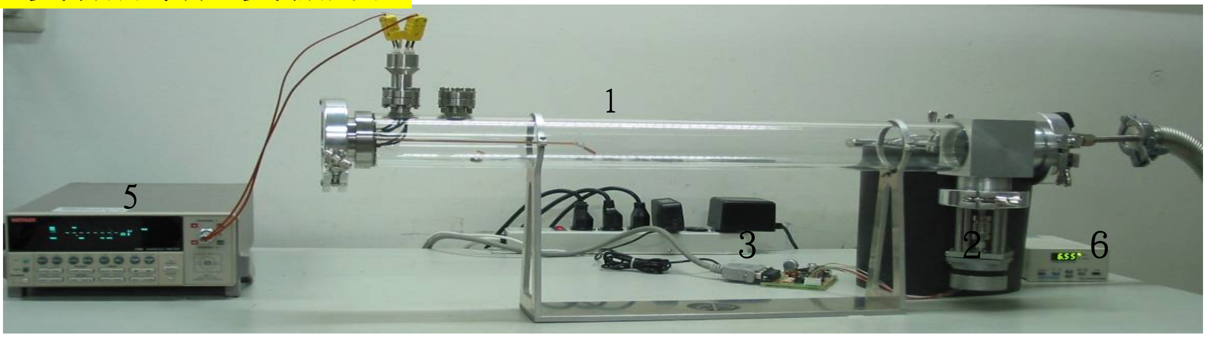
在偶然的機會下發現，當氣球被拉長，在拉伸過程中，氣球溫度明顯上升，若將氣球由伸長狀態縮放回原本狀態，在收縮的過程中也可以明顯感受到氣球溫度下降。然而不清楚此現象是否爲感官上的錯覺，亦或是真實的現象，因此希望以較爲科學的方法，設計一套完整的實驗，並尋找適當的理論來深入探討。

貳、 研究目的

一、 降低樣品與環境間之散熱路徑，並測量其熱傳導係數以爲實驗技術之改進與數據分析之基礎。
二、 探討溫度變化與伸長倍數之函數關係。
三、 探討不同的拉伸速度對溫度變化之影響。
四、 探討不同粗細的橡膠對溫度變化之影響。
五、 探討不同材質的橡膠，是否改變溫度變化與伸長量之函數關係。
六、 降低橡膠的維度是否改變溫度變化與伸長量之函數關係。
七、 由溫度與熵的變化來驗證橡膠的鍵鏈結構。

參、 實驗器材與實驗方法

【圖一】實驗器材裝置圖



一、　**實驗器材：**

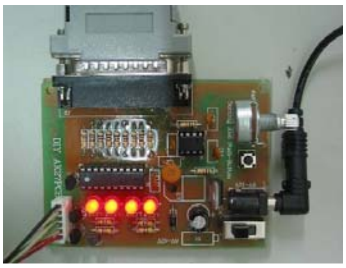
1. 真空管：放置橡膠以隔絕橡膠與外界的熱量傳遞。
2. 步進馬達：等速拉伸橡膠
3. 電路板：為步進馬達與電腦之控制介面。
4. 電腦：控制步進馬達拉伸橡膠的速度，並紀錄溫度的變化。
5. 三用電錶與 K-type 熱電偶(Thermocouple)：量測橡膠的溫度變化。
6. 真空幫浦與真空計。
7. 樣本：橡皮筋、氣球。

二、　**實驗方法：**

1.將橡皮筋裁成適當大小，一端固定於真空管左側蓋上，另一端綁上魚線連接於步進馬達上。熱電偶埋入橡皮筋一端約三公分處，並以 GE 膠固定。

2.減少環境溫度的誤差：調整空調系統保持室內恆溫，啟動幫浦將壓克力管抽真空，令壓力減小至 5 torr 以下。先進行橡皮筋拉伸測試，再以紙箱遮罩整個系統，進一步降低外界聲光的干擾。

3.待系統溫度穩定後開始進行實驗，使用 Labview 撰寫程式控制儀器，以步進馬達等速拉伸和縮放橡皮筋，同時量測並連續紀錄橡膠溫度變化情形。



【圖二】步進馬達裝置圖

【圖三】k-type thermocouple 嵌入橡皮筋

肆、　基本理論與公式

一、熱力學第一定律：

$$dU = dQ + dW \qquad (1)$$

由熱力學第一定律公式，dU 為物體內能之變化， dQ 為熱量之變化， dW

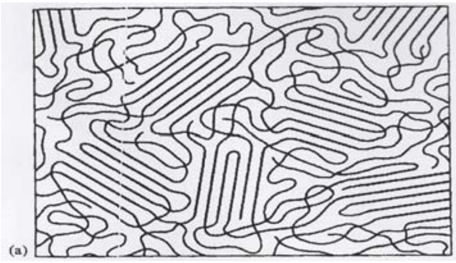
爲外界對物體作的功。

假設在定溫下橡皮筋的內能爲 U ，在固定的溫度下內能不會改變，因此 $dU=0$ 。當拉伸橡皮筋時，外界對橡皮筋作功 dW(正值)，因 $dU=0$， $dQ=-dW$，爲負值，代表橡皮筋會釋放出熱量。

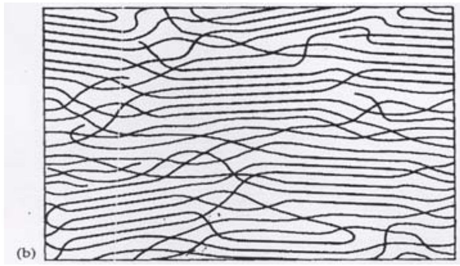
二、 熱量與熵的關係：

$$dQ = TdS \qquad (2)$$

dQ 爲熱能之變化，T 爲系統溫度，dS 爲熵之變化。dQ 與 dS 呈正比關係，比例常數爲 T。



【圖四】拉伸前，橡膠鍵鏈結構排列複雜



【圖五】拉伸時，橡膠鍵鏈結構排列整齊

三、 熵與狀態數的關係：

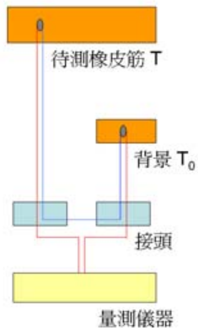
$$S = k_B \ln\Omega \qquad (3)$$

其中 k_B 爲波茲曼常數（Boltzmann's constant= 1.38×10^{23} J /K)

四、 熱量與比熱之關係：

$$dQ = c\,m\,dT \qquad (4)$$

c 爲比熱，m 爲質量。



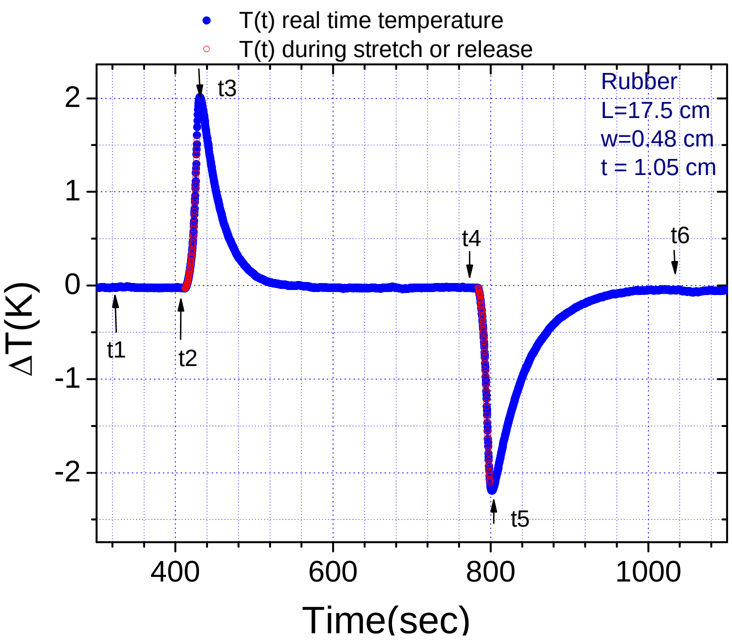
熱電偶裝置示意圖

伍、 實驗結果

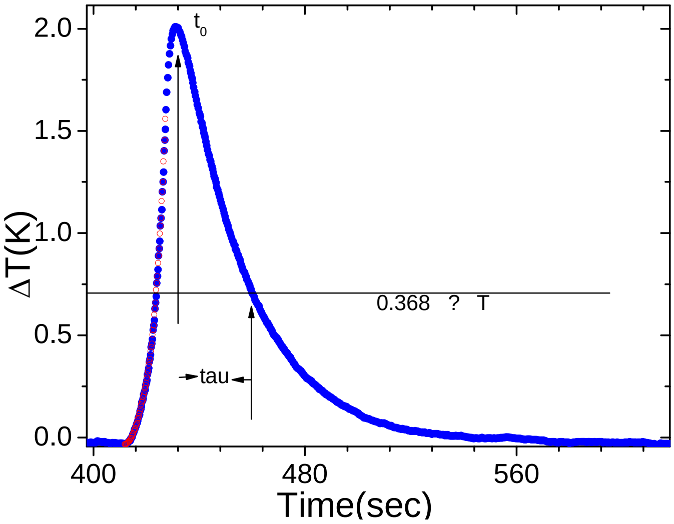
實驗一、　探討溫度變化與伸長量之函數關係。

利用 Labview 自動控制系統，控制步進馬達的轉軸快慢與方向，並自動記錄橡皮筋拉升與縮放過程的溫度變化。爲了精確測量溫度的微小變化，避免受環境溫度漂移之影響，我們使用兩組熱電偶，一組測量橡皮筋溫度 T，一組測量背景溫度 T_0，如【圖六】，由兩者之溫度差如此便可準確的量測到橡皮筋拉升或縮短所造成的溫度變化 $dT=T-T_0$。利用此方法可使溫度穩定性控制在 0.001 ℃/min 以下。

取一橡皮筋(樣品一)由長 13.00 cm，寬 0.24 cm，厚 1.36 cm，以每秒 1.94 cm 拉伸 100%(13 cm)、200%(26 cm)、300%(39 cm)各連續三次，溫度對時間之關係如【圖七】。實驗結果(如【表一】)發現，伸長量越長，溫度變化越趨明顯。推測因伸長量越長，鍵鏈結構狀態變化越大，所產生的熱量也越多。



【圖六】橡皮筋拉伸與縮放， 溫度變化對時間作圖 t1~t2:等待背景溫度穩定，t2~t3:拉伸橡膠，t3~t4:等待熱平衡降溫， t4~t5:縮放橡膠，t5~t6:等待熱平衡升溫



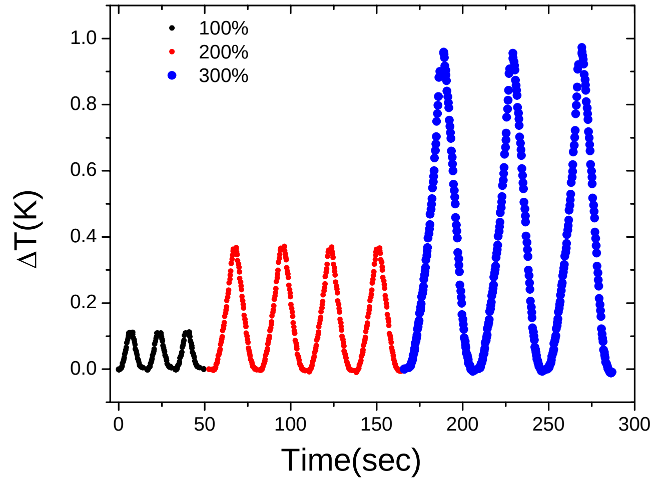
【圖七】橡皮筋拉伸及散熱過程，溫度變化對時間作圖

實驗二：探討溫度變化與伸長量之函數關係。

取一長 13.00 cm 的橡皮筋(寬 0.24 cm，厚 0.155 cm) (樣品一)，以每秒 1.62 cm 拉伸速度，拉伸 13 cm (100%)、 26 cm (200%)、 39 cm (300%)各連續三次，實驗結果溫度對時間之關係如【圖八】 與【表一】) ，可以發現溫度變化與伸長量超越線性函數關係。伸長量越長，溫度變化越趨明顯。推測因伸長量越長，鍵鏈結構狀態數變化越大，所產生的熱量也越多。

【表一】伸長量與拉伸速度的關係

	伸長量 100%	伸長量 200%	伸長量 300%
第 1 次溫度變化（K）	0.1125	0.3699	0.8527
第 2 次溫度變化（K）	0.1103	0.3657	0.8595
第 3 次溫度變化（K）	0.1114	0.3681	0.8629
平均溫度變化（K）	0.1114	0.3679	0.8583



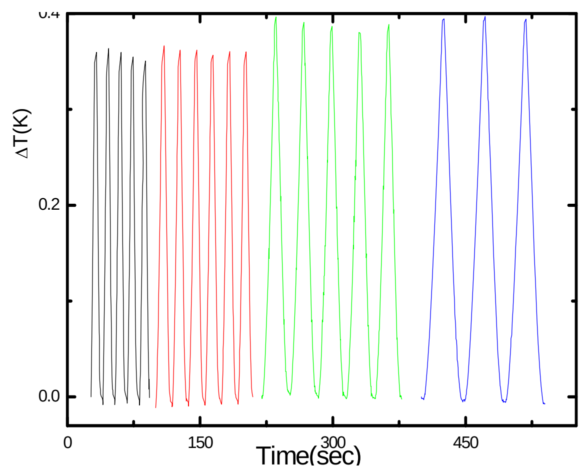
【圖八】橡皮筋連續拉伸與縮放三次，溫度變化對時間作圖

實驗三、探討不同的拉伸速度對溫度變化之影響。

我們發現在不同的拉伸速度下橡皮筋的上升溫度並不盡相同，如【圖九】。實驗結果（如表二）發現，拉伸速度越慢，溫度變化越大，但速度低於 1.62 cm/s 以後即不再明顯變化。推測因速度越快，拉伸時間越短，溫度來不及平衡所致。因此以下實驗均以 1.62 cm/s 之速度拉伸橡皮筋。

【表二】拉伸速度與溫度變化量的關係

拉伸速度（cm / s）	6.5	3.7	1.62	1.13
平均溫度變化 T(K)	0.347	0.356	0.386	0.398



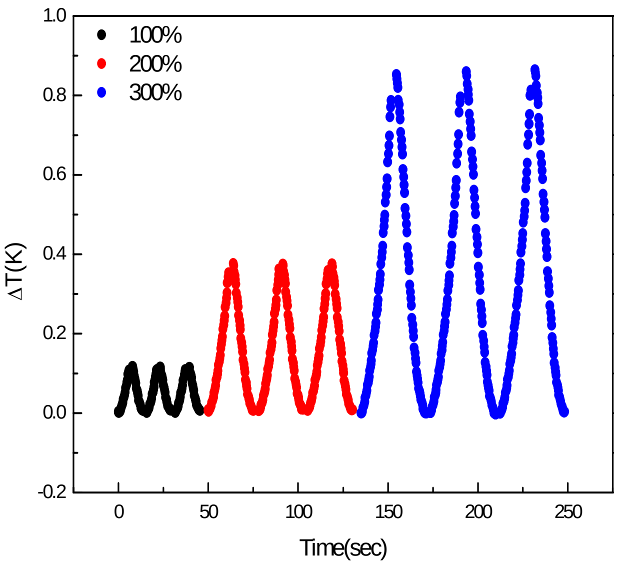
【圖九】相同伸長量，不同拉伸速度下，橡皮筋溫度變化對時間作圖。黑色曲線為拉伸速度 6.5 cm/s，紅色為 3.7 cm/s，綠色為速度 1.62 cm/s，藍色為速度 1.13 cm/s。

實驗四、探討不同寬度的橡膠對溫度變化之影響。

取一橡皮筋（樣品二），寬度為實驗(一)橡皮筋之兩倍(0.48 cm)（長度相同），拉伸 300%，結果如【圖十】，與實驗(一)寬度為 0.24 cm 橡皮筋做比較（表二綠色字體），發現溫度變化非常類似。因 $dQ = -dW$，截面積變成兩倍，外界對橡皮筋作功為 $2\,dW$，同時橡皮筋質量也變為 $2m$，依公式(5)$dQ = c\,m\,dT$，dT不變。此實驗結果進一步證實橡膠分子為長鏈狀結構，鏈鏈結構的橫向交鏈較少，故不太受截面積減半影響。

【表三】兩倍截面積之橡皮筋伸長量與溫度變化量的關係

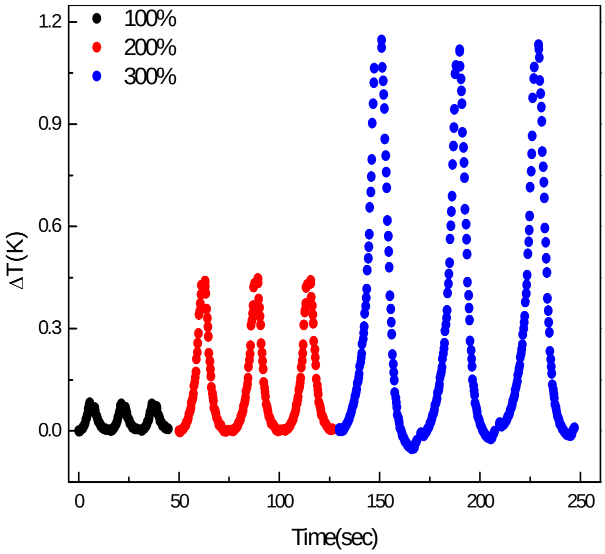
兩倍截面積之橡皮筋	伸長量 100%	伸長量 200%	伸長量 300%
第 1 次溫度變化（K）	0.108	0.366	0.961
第 2 次溫度變化（K）	0.107	0.369	0.942
第 3 次溫度變化（K）	0.109	0.366	0.978
平均溫度變化（K）	0.107	0.367	0.960
橡皮筋（樣品一）			
平均溫度變化（K）	0.0803	0.4426	1.1327



【圖十】兩倍截面積之橡皮筋連續拉伸與縮放三次，溫度變化對時間作圖

實驗五、探討不同材質的橡膠，是否改變溫度變化與伸長量之函數關係。

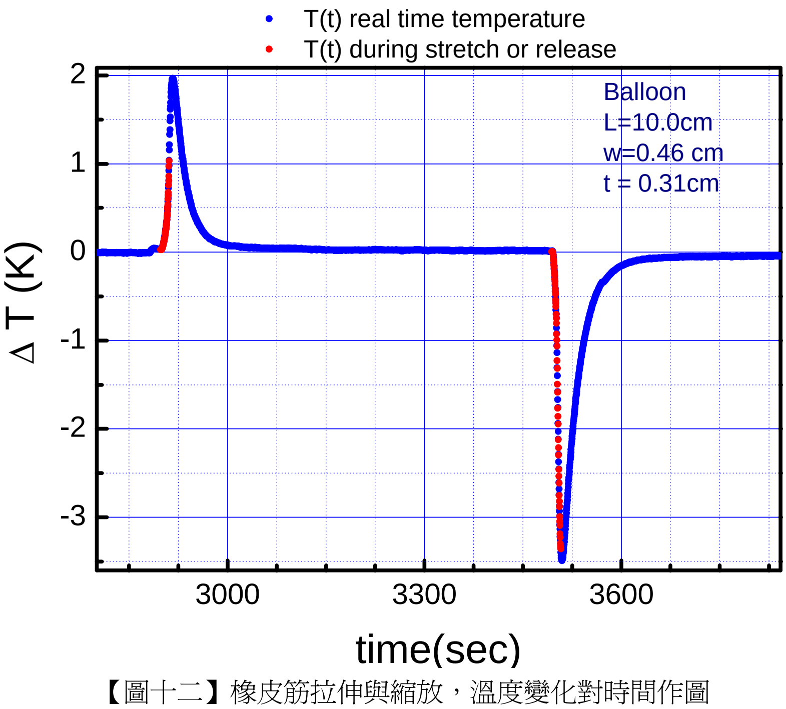
硬度較大的橡皮筋（樣品三），在伸長量為 100%時，溫度變化較軟橡皮筋（樣品二）小，然而伸長量超過 200%後，溫度變化較明顯，如【圖十一】。顯然溫度變化與伸長量的函數關係兩者不同。



【圖十一】橡皮筋連續拉伸與縮放三次，溫度變化對時間作圖

實驗六、降低橡膠的維度是否改變溫度變化與伸長量之函數關係。

取一薄氣球（樣品四）厚度 ~0.031 cm 為實驗(一)橡皮筋之 1/5，拉伸 300%，拉伸完與縮放完後皆予 10 min 之時間等待其逐漸回溫，過程之溫度變化 如【圖十二】 。因氣球厚度較橡皮筋薄，與熱電偶之接觸點更小，造成失真現象越加明顯，而更進一步證實了此散熱現象。



【圖十二】橡皮筋拉伸與縮放，溫度變化對時間作圖

t1~t2:等待背景溫度穩定， t2~t3:拉伸橡膠，t3~t4:等待熱平衡降溫，t4~t5:縮放橡膠，t5~t6:等待熱平衡升溫

陸、 數據分析與討論

一、 橡皮筋與環境之間的熱傳導係數 K 計算：

1.基本放熱理論模型：

當一高溫的物體與環境之間的熱傳導係數為 K，其溫度下降應符合下列函數關係：

$$T(t) = \Delta T e^{-t/\tau}$$

其中，$\Delta T = T_{max} - T_0$ ，T_{max} 為最高溫，T_0 為背景溫度，e 為自然對數，

τ 為放熱時間常數。當 $t=\tau$ ，物體溫度降為 ~ 0.368 ΔT，因此在 T_{max} 與 0.368 ΔT 之時間差即為時間常數 τ 。由【圖七】計算可得 τ = 28 sec

2. 熱容與熱傳導係數及時間常數之關係：

依照比熱量測理論 $C = k\tau$

其中，C 為熱容，k 為熱傳導係數，τ 為時間常數。

3. 散熱造成之誤差計算：

依【圖七】，由開始放熱至放熱結束約需 108 秒，溫度下降 2℃，散熱速度為－0.012(℃/s)。由實驗可得橡皮筋拉伸約需 18 秒，即拉伸過程中溫度下降 0.213 ℃，其造成誤差約 11%。

4. 樣品與環境熱傳導係數 K 的探求：

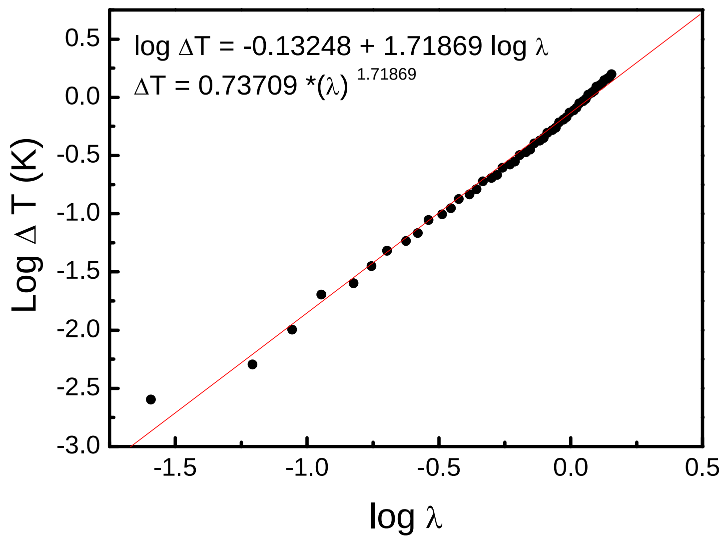
橡皮筋質量 m = 0.0154 g，比熱 c =1.46 J/g℃，τ 時間常數為 28 sec，由 $C=mc=k\tau$ ，可估計出 Thermocouple 之熱傳導係數 $k = 8.03 \times 10^{-4}$ J/sec℃

三、 以拉伸前後狀態數Ω的改變，驗證橡膠的鍵鏈結構：

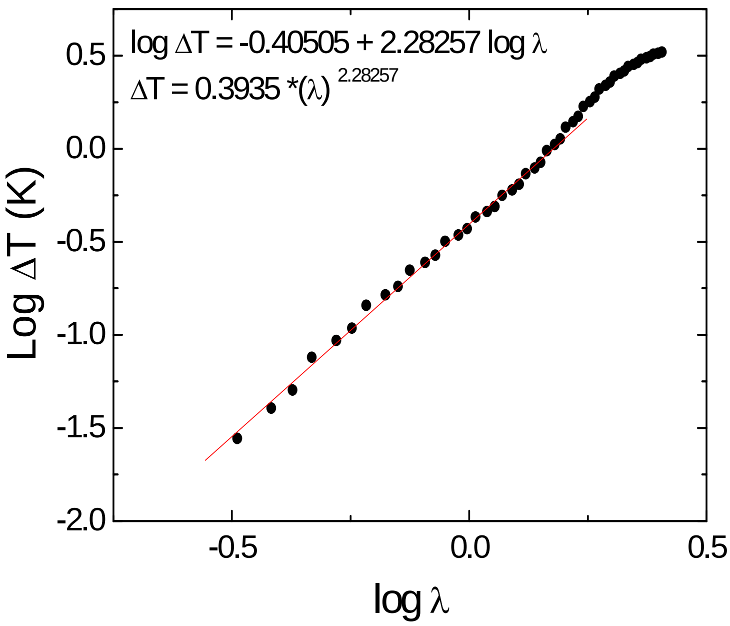
由 $dQ = mc\Delta T$ 算得 dQ=－4.5 J，進一步由 $dQ = TdS$ 算得 dS=-3×10^{-2} J/K ，由公式(3) $S = k_B \ln\Omega$ 推出 $dS = S_f - S_i = R \ln \Omega_f/\Omega_i$ ，計算出拉伸時較拉伸前之狀態數變化 $\Omega_f/\Omega_i \sim 0.97$

四、 溫度變化量 △T 與伸長倍數λ的函數關係：

設 $\Delta T = a(\lambda)^X$ ，兩邊同取對數可得 $\log \Delta T = \log a + x \log(\lambda)$，在樣品三的數據中，log a = －0.13，$X$=1.72，如【圖十三】所示。氣球的 log a = －0.41，X=2.28 如【圖十四】所示，此一函數的理論模型，更待進一步推導與確認。



【圖十三】橡皮筋(樣品三)的△T 1 與 λ 的對數關係圖



【圖十四】氣球(樣品四)的△T 與 λ 的對數關係圖

柒、 結論

一、橡皮筋伸長量與溫度變化之關係：

橡膠溫度變化與伸長量超過線性關係，推測由於伸長量加大，鍵鏈結構排列狀態改變量急速增加，溫度變化也隨之越加明顯。

二、拉伸速度與橡皮筋溫度變化之關係：

拉伸速度越慢，溫度變化越明顯，但速度低於 1.62 cm/s 以後即達到穩定。推測由於橡膠拉伸速度越快，熱電偶與橡膠溫度來不及平衡所致。

三、橡皮筋截面積與溫度變化之關係：

截面積改變對溫度變化沒有太大影響，證實橡膠內單位體積內的的鍵鏈結構

密度分布均勻。

四、不同硬度之橡皮筋材質對於其溫度變化之影響：

硬度較大的橡皮筋，在伸長量為 100%時，溫度變化較軟橡皮筋小；當伸長量超過 200%後，溫度變化較明顯。由此可知，橡膠溫度變化與伸長量的函數關係兩者相異，其物理意義更待進一步探討。

五、探討橡膠的厚薄是否改變溫度變化與伸長量之函數關係：

相同伸長倍率之下，厚度較薄的氣球溫度變化量較大。用 $\triangle T=a(\lambda)x$ 式子來描述橡皮筋之溫度變化量 $\triangle T$ 與伸長倍數 λ 的函數關係，發現氣球指數 x=2.28 明顯大於橡皮筋 x=1.72，其物理意義更待進一步探討。

捌、參考資料

1. L. R. G. Treloar, The Physics of Rubber Elasticity, Oxford University Press(2005)

2. Xiangjun Xing,Paul M.Goldbart, Leo Radzihovsky (Feb.2007) ,Thermal Fluctuations and Rubber Elasticity,Phys.Rev.Lett.98,075502.

3. S.L.Dart,R.L.Anthony,Eugene Guth(1943),Rise of Temperature on Fast Stretching of Synthetics and Natural Rubbers,Industrial and Engineering Chemistry, Vol.34, No.113,P.1340~1342.

評語

實驗分析及理論說明都相當完整，符合科學過程技能。創新的構想也頗值得嘉許。

Correlation between Thermal Behavior and Molecular Network in Rubber

Yun-Chu Wang

I. Introduction

When playing a balloon, I found some interesting things which I have never expected. For examples, the temperature of balloon will change if it under stress; the temperature change is dependent on the structural deformation and material; temperature rise and fall are different when stretched and releases respectively. With the help of delicate measuring electronic tools and automatic data acquisition I confirmed some problems which are debatable in the past and had better insights for these phenomena.

II. Objects

1. Confirm the molecular structure of rubber.
2. Try to find an universal equation to describe the relationship between temperature change and stretch ratio.
3. Understand the physical mechanism to explain the time-lag effect and asymmetric temperature change.

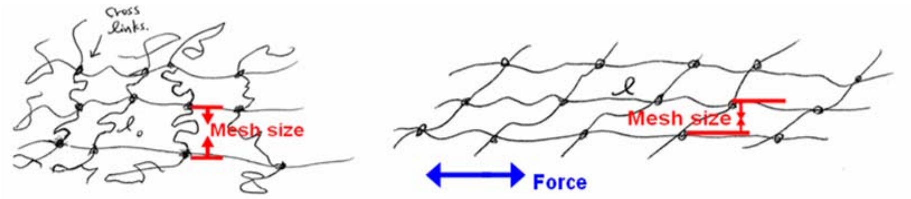


Fig. 1 The rubber structure array (left) before and (right) after stretching.

III. Materials and methods

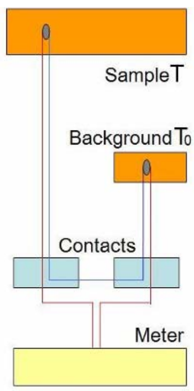


Fig. 2 A pair of thermocouple inserted into the rubber (left); the differential method for temperature measurement ΔT with precision ~0.001℃.

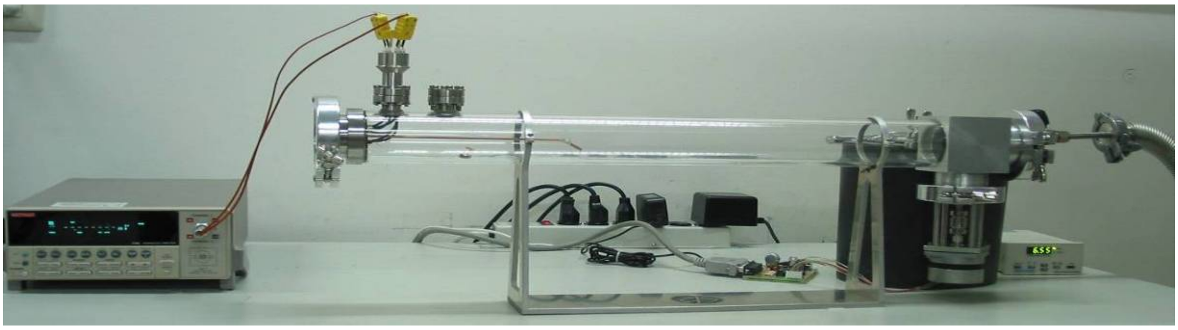


Fig. 3 (1)Thick-wall acrylic tube (2) Stepping motor (3) Circuit board (4) Ammeter and thermocouple (5) Vacuum gauges and (6) Vacuum pump

Experimental procedures

Fix one end of the specimen and tie the other end to a stepping motor (Fig. 3), and then start the stepping motor with a fixed speed to stretch the specimen. By reversing the direction of stepping motor, the specimen is released. The temperature change versus time is monitored by thermocouples and infrared detector.

IV. Results

Experiment 1. Reduce the thermal link of specimen from environment.

(a). With air in the acrylic tube, a rubber band is stretched to twice of its length ($L = 2L_0$), i.e. $\lambda = 2$. The temperature of the rubber increases from its initial temperature (T_0) to a final temperature (T_f). After stretching the temperature of rubber starts to decrease exponentially to T_0 with a time constant τ = 25.8 s. This indicates there is heat transfer between the specimen and the environment.

(b). Then pumped the acrylic tube to vacuum, repeat the experiment, the temperature of rubber still decreased exponentially to T_0 but with τ =29 s. Since the rubber was suspended in vacuum, the thermal contact is concluded to be due to the thermocouple. Vacuum did improve the thermal isolation but the thermal link of thermal couple cannot be avoided.

Remark: The thermal relaxation of a specimen can be described by the formula

$$\Delta T(t) = \Delta T(0)\, e^{-t/\tau}$$

Where $\Delta T(0)$ is the peak temperature change, τ is the time constant. K is thermal conductivity of thermal link between specimen and environment.

Take $\ln \Delta T(t) = \ln \Delta T(0) - (1/\tau)\, t$, the value of τ can be calculated from the slope of linear fit in Fig. 4.

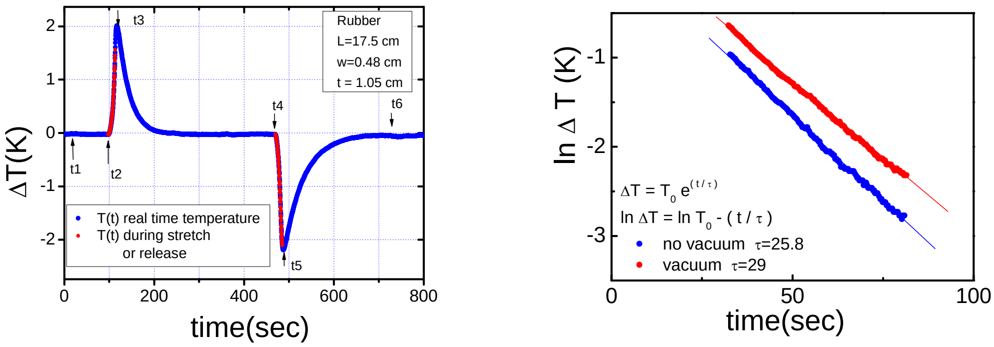


Fig. 4 The temperature change versus time for stretching and releasing the rubber (left); the log (ΔT) vs. t for in air and in vacuum (right).

t_1 - t_2: before stretch, t_2 - t_3: temperature rise during stretch, t_3 - t_4 and t_5 - t_6 : thermal relaxation region, t_4 - t_5: temperature cools down during relaxation.

Experiment 2. Explore the relation of temperature change ΔT with stretch ratio (λ) by fitting to equation $\Delta T = a\ (\lambda - 1)^x$, where *a* is a constant and *x* is the exponent.

A rubber band with L_0 = 13 cm is stretched to stretch ratio λ = 2, 3, and 4 respectively (Fig. 5). Fit the data to above Equation, the fit gives ***a*** = 0.13 and ***x*** = 1.63.

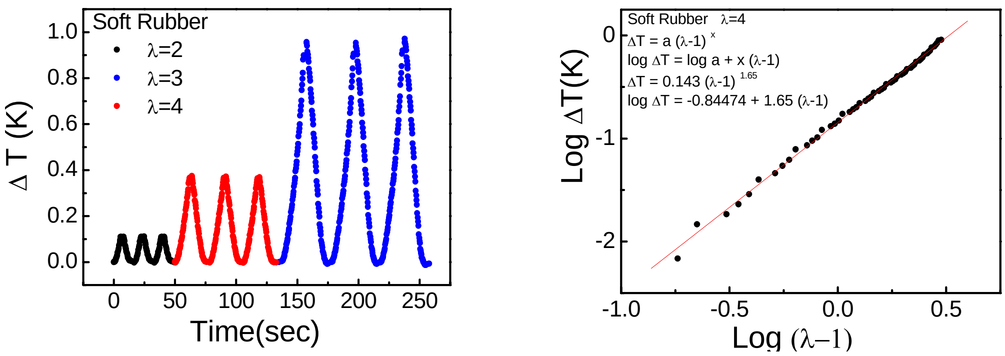


Fig. 5 ΔT(t) for stretch and release with λ = 2, 3, and 4 (the left) . Fitting the data to *log* $\triangle T = \log a + x \log (\lambda - 1)$

Experiment 3. Study the hardness dependence of the functional ΔT(λ) for soft rubber and hard rubber.

Repeat the experiment 2 with a stronger rubber band. We found the temperature change for hard rubber is larger than the soft one. The fitting values ***a*** and ***x*** are listed in Table below.

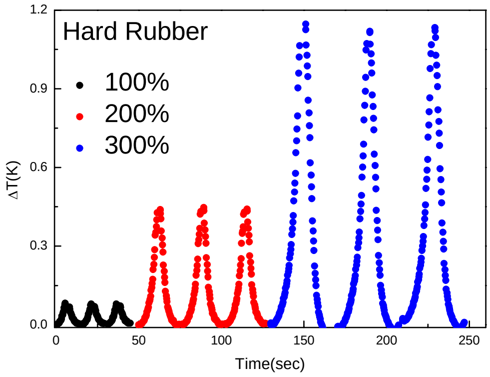


Fig. 6 ΔT vs. time for hard rubber with λ = 2, 3 and 4

	Average ΔT	a	x
Soft rubber	0.96	0.143	1.65
Hard rubber	1.132	0.0545	2.43
Balloon	1.89	0.142	2.32

Table 1. The values of *a* and *x* for different specimens by fitting $\Delta T = a(\lambda-1)^x$

Experiment 4. The unusual behaviors observed in balloon specimen.

Repeat experiment 2 with a thinner wall balloon with thickness ~ 0.3 mm. Three characteristics were observed. (1) A time lag for the temperature rise (red curve in Fig 7 left). (2) Temperature rise and fall are unequal. (3) Temperature change of balloon is much larger than that in rubber (Table 1).

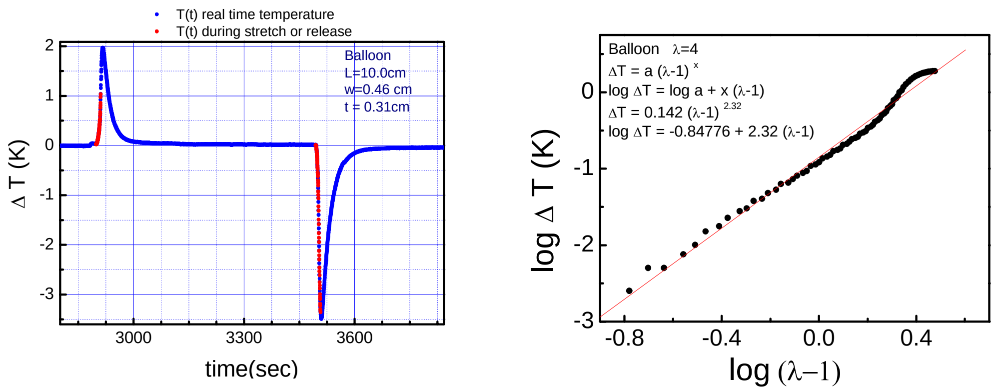


Fig. 7 ΔT versus time, the red data taken during stretching and restoration (left); Log (ΔT) versus log (λ - 1) (right).

Experiment 5. Using a non-contact method to measure ΔT and confirm the time lag and the asymmetric temperature change.

In order to confirm the results above, a non-contact temperature change is measured with an infrared detector. The time lag and asymmetry of temperature change are observed as well, confirming these results.

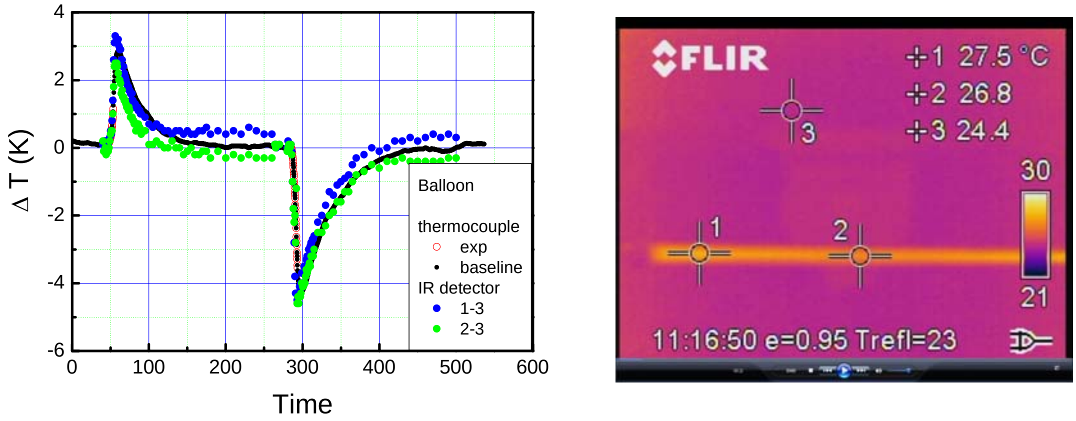


Fig. 8 Data taken by infrared detector. The black line is the data from thermal couple, blue dots and green dots are the temperature difference measured at positions 1 and 2 refer to reference position 3 (background) respectively.

V. Data Analyses and Discussions

1. The thermal conductivity *K* of the thermal link between specimen and environment

The relation of heat capacity (***C***), thermal conductivity (***K***), and the time constant (τ) can be formulated as $C = K\tau$. Assuming the rubber mass (***m***) is 145.9 g, the specific heat of rubber ***c*** is 1.46 J/g K, with $C = mc$ and $\tau = 29$ sec, the ***K*** is estimated to be **1.49x 10^{-3}** J/s K.

2. Estimate the released heat (*dQ*) and the reduction of entropy change (*dS*) inrubber after stretched.

The released heat ***dQ*** can be calculated from $dQ = cm\Delta T$. With ***c*** = 1.46 J/g K and ***m*** = 145.9 g, the heat ***dQ*** is calculated to be ~204.5 J. Since the heat is released from the reduction of entropy change $dQ = T\,dS$. The entropy change $dS = dQ / T$ = 2.78 x10^{-3} J/K. From Eq. (2) $dS = 13(m / M)NR\ ln(\Omega_f / \Omega_i)$, where ***M*** is the molecular weight, ***N*** is the Avogadro constant, and ***R*** is the gas constant, the ratio of number of states before and after stretching (Ω_f / Ω_i) to be ~0.993.

3. The relation of temperature change ΔT and stretch ratio (λ) represented by formula $\Delta T = a(\lambda-1)^x$

The three specimens (soft rubber, hard rubber and balloon) are well fitted to the empirical formula $\Delta T = a(\lambda-1)^x$. ***a*** is the proportionality constant between ΔT and entropy change. The exponent ***x*** relate to the number of states change (or entropy) under the stretch deformation. We found balloon has the largest value of ***a*** and ***x*** in three samples (Table 1), ***a*** and ***x*** are correlated to the characteristics of the structure of the polymer network in the specimen. The specimen has smaller mesh size will have larger temperature change (discussed below).

4. The mesh size of the polymer network (ξ) through the elastic free-energy density (f_0)

Based on Eq. (3), $\boldsymbol{f_0 = K_B\, T\, ln(\Omega_f / \Omega_i) / V}$, and Eq. (4), $\boldsymbol{f_0 = (1/2)\, K_B\, T / \xi^3 (\lambda^2 + 2/\lambda)}$, the mesh size can be obtained from $\boldsymbol{dS}$ and functional $\boldsymbol{f_0 (\lambda)}$. From Fig. 9, the mesh size of balloon and soft rubber are estimated to be 2 nm and 3 nm respectively. It is known that the classical theory does not work well for experiment data [2]. Its failure can be observed in the Mooney-Rivlin plot of the stress-strain relation, taking the derivate $\boldsymbol{df / d\lambda = K_B\, T / \xi^3 (\lambda - \lambda^{-2})}$ and plot mesh size versus $\boldsymbol{(\lambda - \lambda^{-2})}$. For the case of balloon, our data shows the mesh size decreases as stretch ratio λ increase, the result is opposite previous report by Xing et al.[2]. The inconsistency may be due to the difference in the materials.

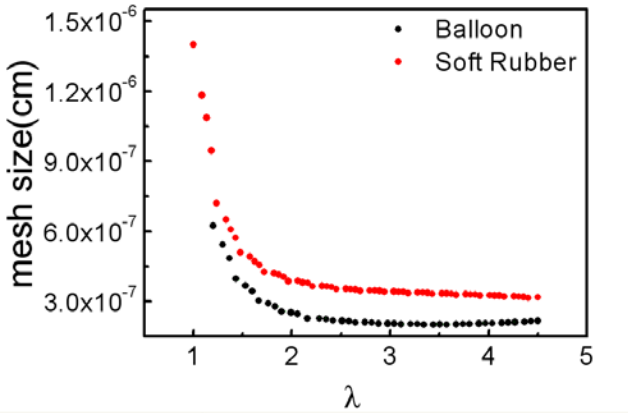


Fig. 9 Estimated mesh size versus λ.

5. The explanation for time-lag effect and the asymmetry in temperature rise and fall

The time-lag could be explained by the formation of localized crystalline structure within small regions of the rubber band [3]. It is known that stretching reduces the entropy of the polymer and increases its melting temperature. This could lead the free polymers to align and freeze within the rubber band. Freezing would release further heat and lead to a further increase in temperature after the specimen is stretched. Similarly, a melting transition to lead to a further decrease in the temperature after the specimen is restored to its native length. The asymmetry is also due to some change in the polymer network structure, it disappears after the rubber band is stretched after approximately 3 times, as shown in Fig. 10.

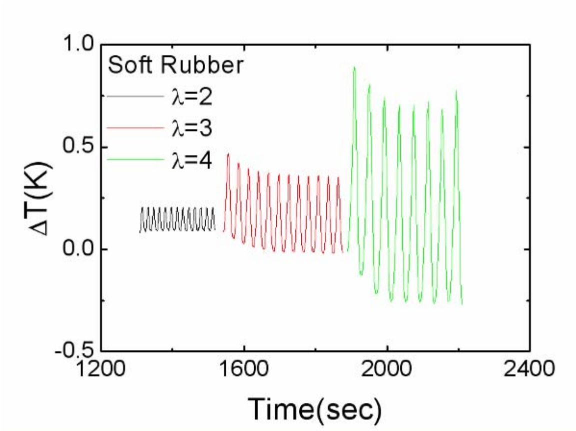


Fig. 10 Temperature change of soft rubber

VI. Conclusions

1. Comparison of anomaly on different materials:
   (1) Time-lag effect and asymmetric temperature change are observed in all specimens after stretching.
   (2) These effects are more obvious in balloons than in rubbers.
2. An universal equation to describe the temperature change with stretch ratio:

$$\Delta T = a(\lambda - 1)^x$$

3. Mathematical validation of rubber molecular structure:
   (1) The number of states after stretching is confirmed via experiment.
   (2) The mesh size isn't a constant when stretched.
   (3) The mesh size of rubber is larger than that of balloon. This result may indicate the different effects on time-lag and asymmetry in temperature change.

VII. References

[1] L. R. G. Treloar, The Physics of Rubber Elasticity, Oxford University Press (2005) *http://www.doitpoms.ac.uk/tlplib/stiffness-of-rubber/index.php*

[2] X. Xing, P. M.Goldbart, L. Radzihovsky ,"Thermal Fluctuations and Rubber Elasticity", Phys. Rev. Lett. **98**, 075502. (2007)

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