Rubber Thermodynamics

Thermodynamics applies to many systems!

Example use thermodynamics to understand the properties of **elastic materials**, such as rubber

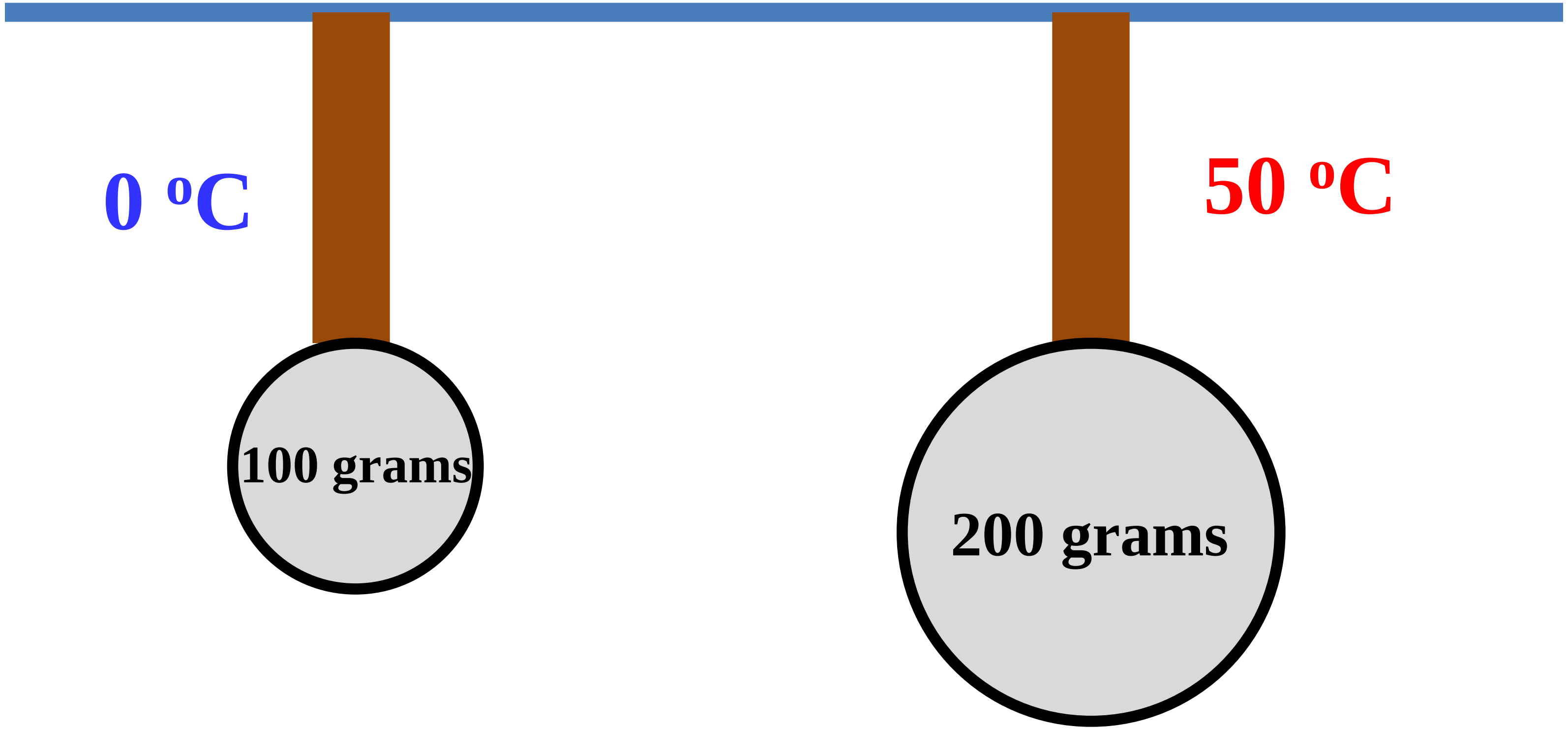
Puzzles: Adiabatic expansion of a gas causes cooling.
Adiabatic compression of a gas causes warming.
But elastic materials show the ***opposite behavior***:

- adiabatically **stretching a rubber band increases its temperature**

- adiabatically **contracting a rubber band decreases its temperature**

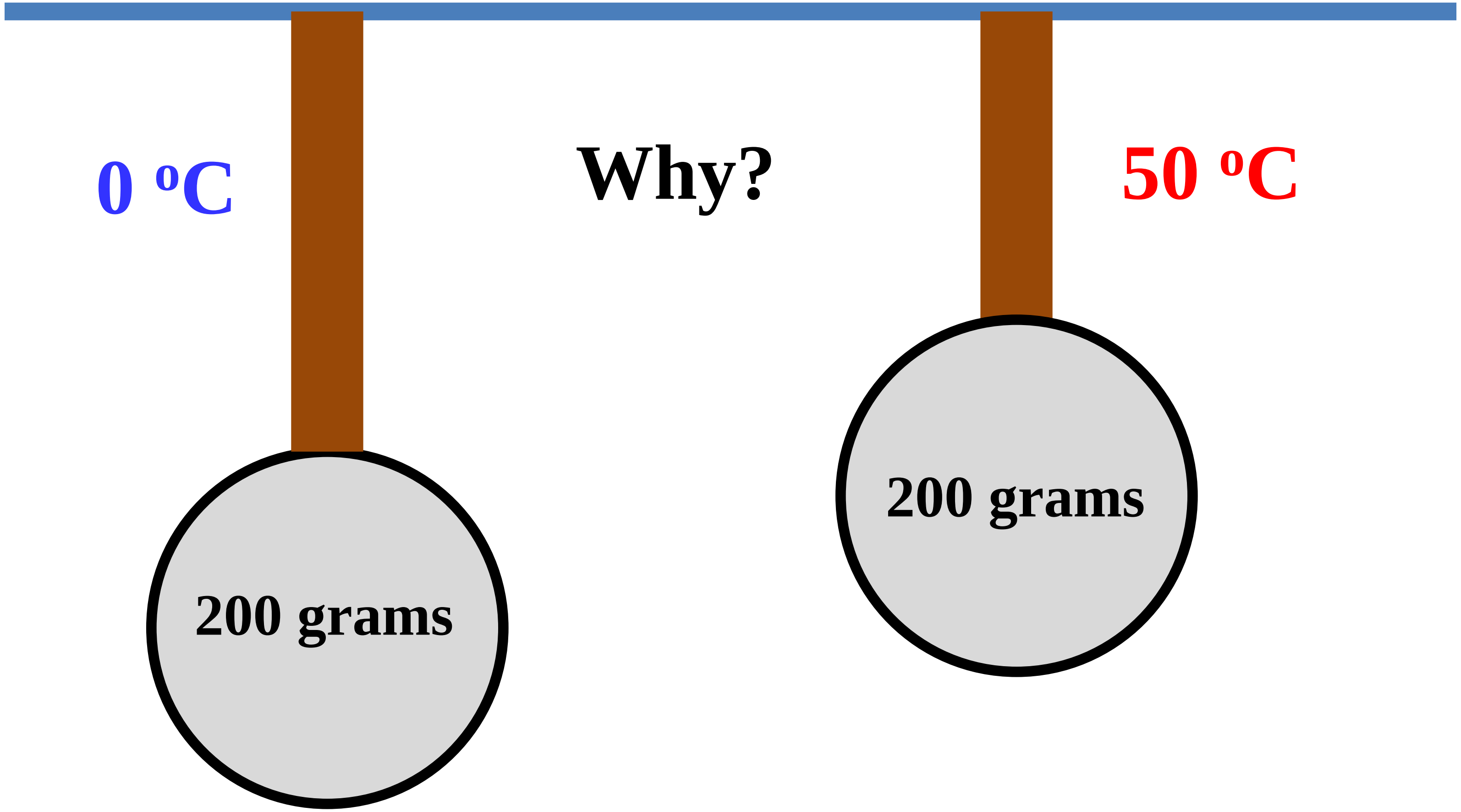
Rubber Thermodynamics

- heating a rubber band makes it stronger, allowing it to carry more weight for the same extension



Rubber Thermodynamics

- heating a rubber band makes it stronger, requiring less extension to carry the same weight



Rubber Thermodynamics

First Law

$$dU = dq - \cancel{p_{ext}dV}^{\,0} + f\,dl$$

$$\boxed{dU = dq + f\,dl}$$

dq = **heat added**

$-\,p_{ext}dV$ = **compression/expansion work** (negligible because the band volume is very small and nearly constant)

$f\,dl$ = **tension work** required to stretch the band from length l to length $l + dl$ against **restoring force *f***

Rubber Thermodynamics

Tension Work

tension work = force f acting over distance dl

$$= f\,\mathrm{d}l$$

Tension Force: Hooke's Law

$$f = k(l - l_{eq})$$

k = force constant

$l - l_{eq}$ = displacement from un-stretched length l_{eq}

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Second Law

For a reversible process ($dq = TdS$):

$$dU = TdS + fdl$$

Helmholtz function (more convenient):

$$\begin{aligned} dA &= d(U - TS) \\ &= dU - d(TS) \\ &= dU - TdS - SdT \\ &= TdS + fdl - TdS - SdT \\ &= -SdT + fdl \end{aligned}$$

$$dA = -SdT + fdl$$

Rubber Thermodynamics

Second Law

Helmholtz function

$$\mathrm{d}A = -S\,\mathrm{d}T + f\,\mathrm{d}l$$

$$\mathrm{d}A = \left(\frac{\partial A}{\partial T}\right)_l \mathrm{d}T + \left(\frac{\partial A}{\partial l}\right)_T \mathrm{d}l$$

first derivatives

$$-S = \left(\frac{\partial A}{\partial T}\right)_l \qquad f = \left(\frac{\partial A}{\partial l}\right)_T$$

Maxwell relation:

$$\left[\frac{\partial}{\partial l}\left(\frac{\partial A}{\partial T}\right)_l\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial l}\right)_T\right]_l$$

gives

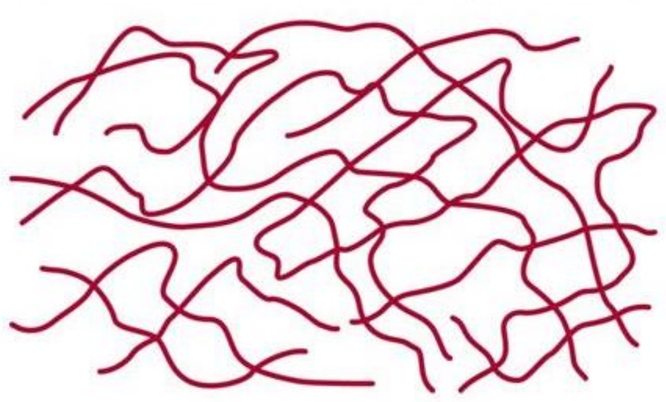
$$-\left(\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial f}{\partial T}\right)_l$$

Rubber Thermodynamics

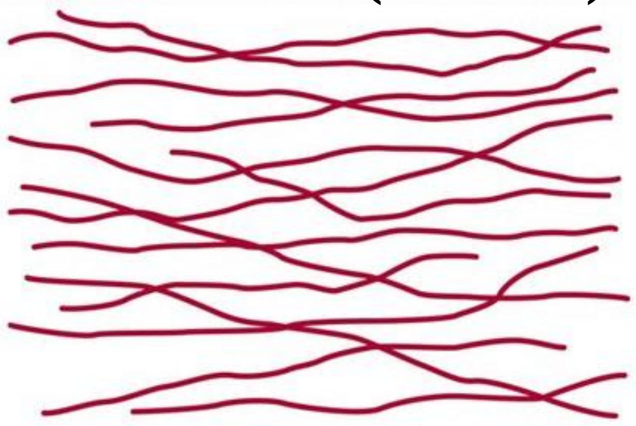
Molecular Interpretation

Natural rubber is a tangled 3-dimensional web of high molecular weight poly(*cis*-isoprene) chains. Stretching the rubber aligns the polymer chains, produces more order and decreases the entropy.

unstretched (higher *S*)



stretched (lower *S*)



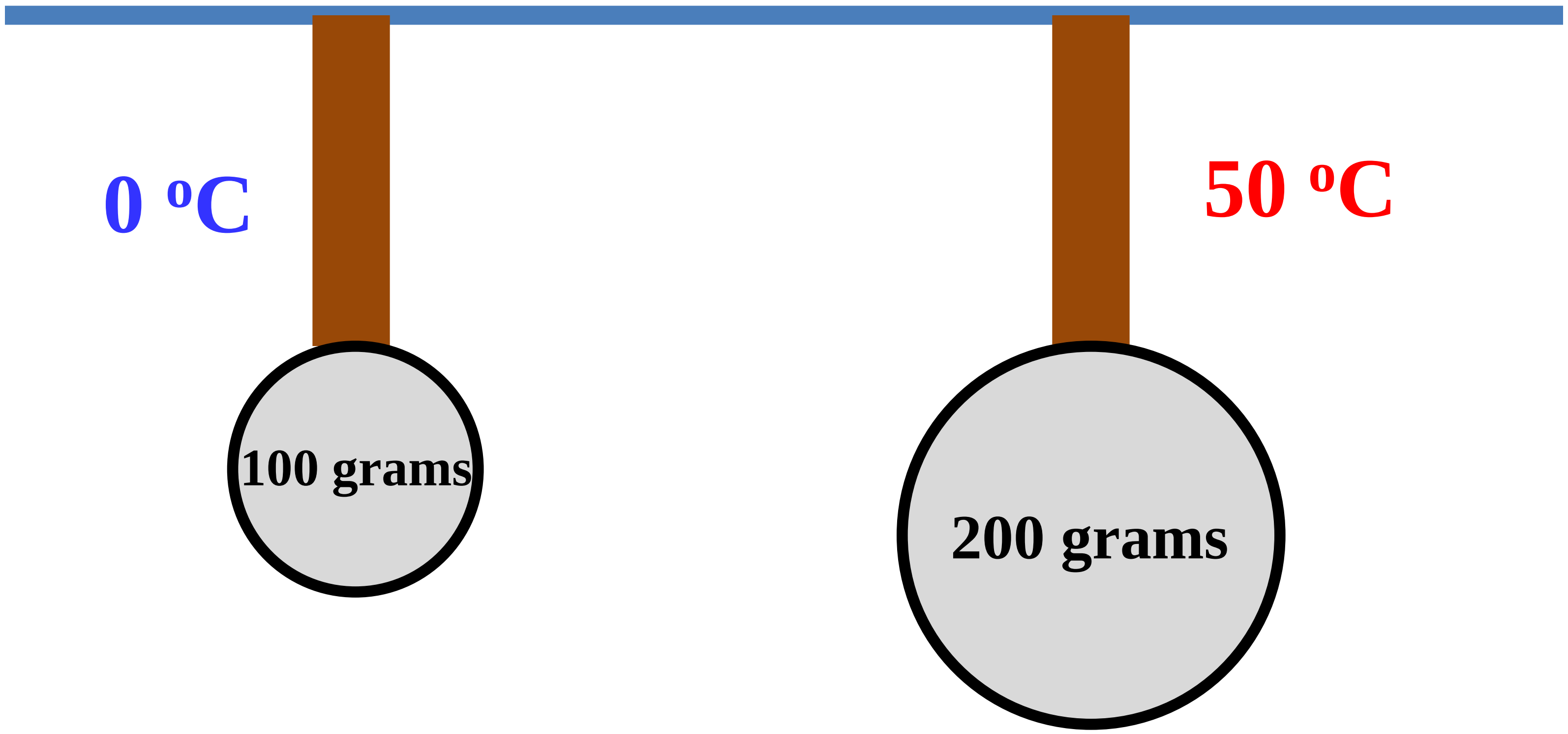
$$\left(\frac{\partial S}{\partial l}\right)_T < 0$$

$$\left(\frac{\partial f}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T > 0$$

Rubber Thermodynamics

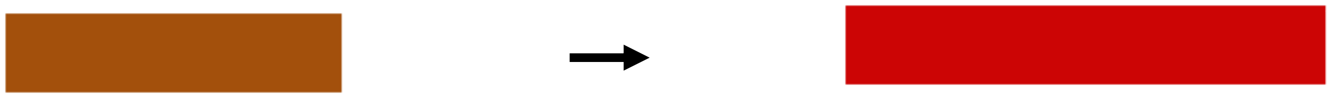
$(\partial f / \partial T)_l > 0$

heating a rubber band makes it stronger, allowing it to carry more weight for the same extension



Rubber Thermodynamics

Stretch a Rubber Band - it warms up



A Contracting Rubber Band Cools Down

Why?

Rubber Thermodynamics

Cyclic Rule

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_l \left(\frac{\partial T}{\partial l}\right)_S$$

$$= -\frac{T}{T}\left(\frac{\partial S}{\partial T}\right)_l \left(\frac{\partial T}{\partial l}\right)_S$$

$$= -C_l \left(\frac{\partial T}{\partial l}\right)_S$$

C_l = **heat capacity** of the rubber at fixed extension

Rubber Thermodynamics

$$\left(\frac{\partial S}{\partial l}\right)_T = -\frac{C_l}{T}\left(\frac{\partial T}{\partial l}\right)_S$$

$$\left(\frac{\partial S}{\partial l}\right)_T < 0 \qquad\qquad C_l > 0$$

$$\left(\frac{\partial T}{\partial l}\right)_S = -\frac{T}{C_l}\left(\frac{\partial S}{\partial l}\right)_T > 0$$

Rubber bands warm up with stretching,
cool down when contracting.