Lecture 17. *Rods, bubbles, and magnets*

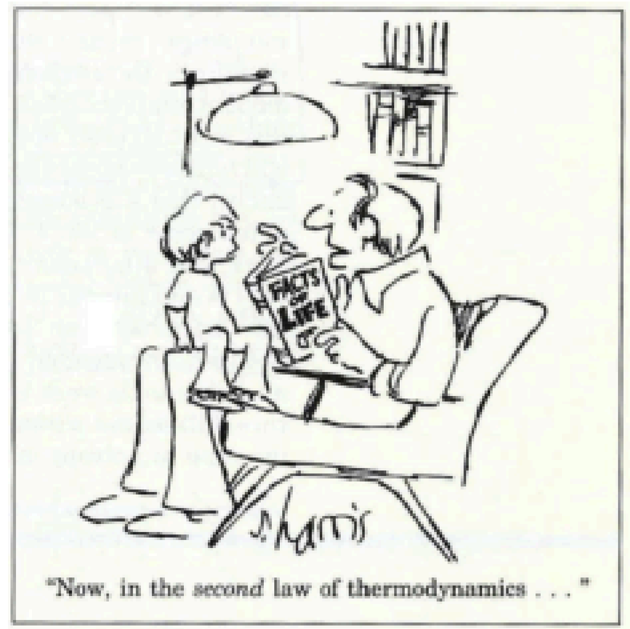
- Work in various situations
- Heat and entropy changes

General expression for work

$$\text{đ}W = X\,\mathrm{d}x$$

Generalized force → X

Generalized displacement → $\mathrm{d}x$



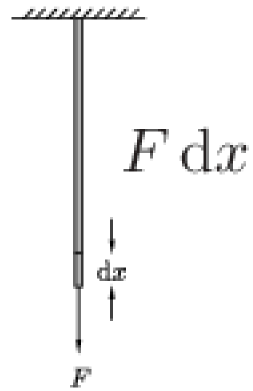
From the *New Yorker*

General expression for work

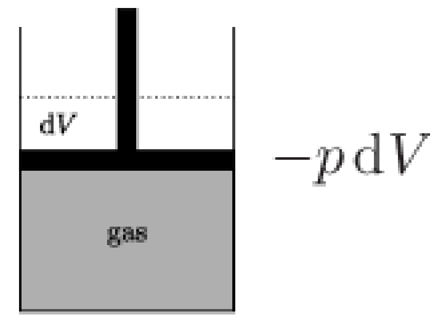
$$đW = X\,\mathrm{d}x$$

Generalized force (X)

Generalized displacement ($\mathrm{d}x$)



Stretching a wire



Compressing a gas

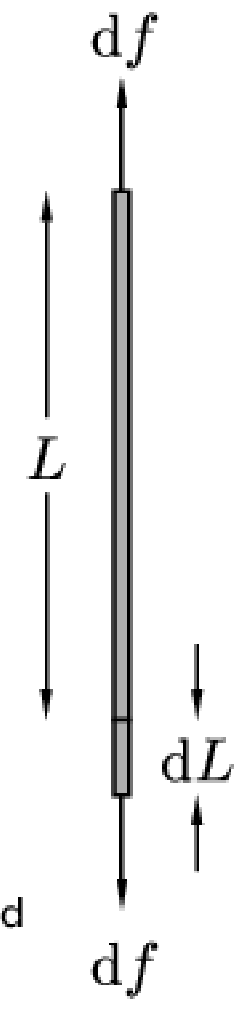
Elastic Rod

Rod with cross-sectional area A and length L, held at temperature T.

The rod is made from **any elastic material** (such as a metal or rubber) and is placed under an infinitesimal tension $\mathrm{d}f$ which leads to the rod extending by an infinitesimal length $\mathrm{d}L$.

Isothermal Young's modulus E_T: ratio between (uniaxial stress; or load) $\sigma = \mathrm{d}f/A$ to strain $\epsilon = \mathrm{d}L/L$:

$$E_T = \frac{\sigma}{\epsilon} = \frac{L}{A}\left(\frac{\partial f}{\partial L}\right)_T$$



The Young's modulus E_T is always a positive quantity.

Young's modulus measures the stiffness of the material; the amount of stress needed to yield a given deformation.

Linear expansivity at constant tension

Linear expansivity at constant tension, α_f:

$$\alpha_f = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_f$$

which is the fractional change in length with temperature.

This quantity is positive in most elastic systems (notable exception rubber).

If you hang a weight onto the end of a metal wire (thus keeping the tension f in the wire constant) and heat the wire, it will extend. This implies that $\alpha_f > 0$ for a metal wire.

For rubber, the same procedure will make it contract, and thus $\alpha_f < 0$ for rubber.

Change of tension of a wire held at constant L with T?

$$\left(\frac{\partial f}{\partial T}\right)_L = -\left(\frac{\partial f}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_f = -AE_T\alpha_f$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

Back to thermodynamics

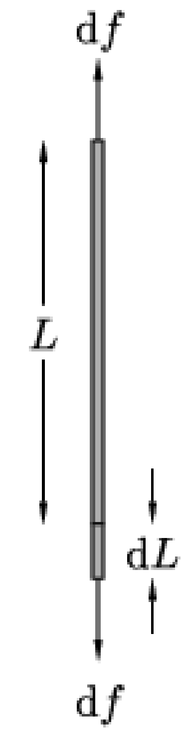
Internal energy: $\mathrm{d}U = T\,\mathrm{d}S + f\,\mathrm{d}L$

Helmholtz free energy: $\mathrm{d}F = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T$

$$\mathrm{d}F = -S\,\mathrm{d}T + f\,\mathrm{d}L$$

Entropy: $S = -\left(\frac{\partial F}{\partial T}\right)_L$

Tension: $f = \left(\frac{\partial F}{\partial L}\right)_T$



$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

Heat and Entropy

Maxwell relation: $$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L$$ Isothermal change in entropy

$$\left(\frac{\partial S}{\partial L}\right)_T = AE_T\alpha_f,$$ Stretching the rod increases the entropy if $\alpha_f > 0$

For an ideal gas, we saw: $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V > 0$$

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

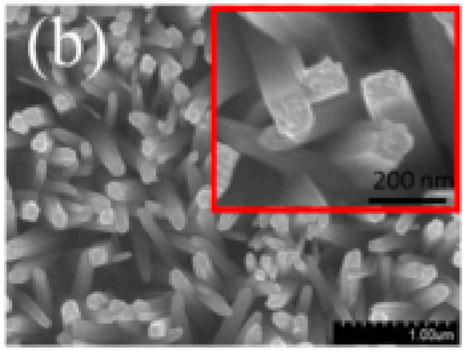
$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right)$$

Increased entropy at constant T means that heat must be absorbed!

$$\Delta Q = T\Delta S = AE_T T\alpha_f \Delta L$$ (isothermal and reversible stretching)

Why is entropy going up?

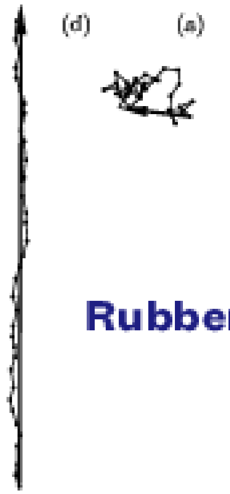
$$\Delta Q = T\Delta S = AE_T T\alpha_f \Delta L$$



SEM image of the TiO2 rods
from Materials **2017**, 10(7), 778

A metallic wire is made of many small crystallites
(each with low entropy — why?)

Stretching the wire distorts the crystallites, which then increase their entropy and so heat is absorbed



Rubber

This is different for rubber, made up of long atomic chains, stretching them **decreases** the entropy: heat is thus emitted when isothermally extended!

Changes of U in an isotherm when a rod is elongated?

This is the sum of a positive term expressing the energy going into the rod by work and a term expressing the heat flow into the rod due to an isothermal change of length.

Note: for an ideal gas, a similar analysis applies, but the work done by the gas and the heat that flows into it balance perfectly, so that U does not change.

Reminder: for an ideal gas, $dU = 0$ (only depends on T)

Surface tension

$$đW = \gamma \, \mathrm{d}A$$

Work to create a surface dA

https://www.colourbox.com/image/water-droplets-on-mettallic-surface-image-3690606

Piston moves down: work done $đW = F\,\mathrm{d}x = +p\,\mathrm{d}V$
(Incompressible liquid)

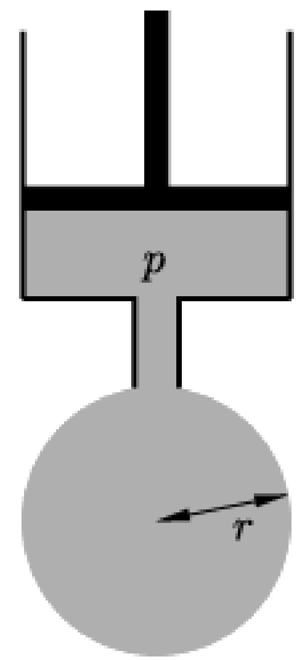
Droplet volume change: $\mathrm{d}V = 4\pi r^2\,\mathrm{d}r$

Surface area: $\mathrm{d}A = 4\pi(r+\mathrm{d}r)^2 - 4\pi r^2 \approx 8\pi r\,\mathrm{d}r$

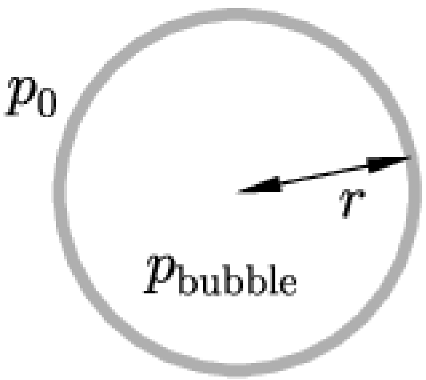
Work to create that surface: $đW = \gamma\,\mathrm{d}A = 8\pi\gamma r\,\mathrm{d}r$

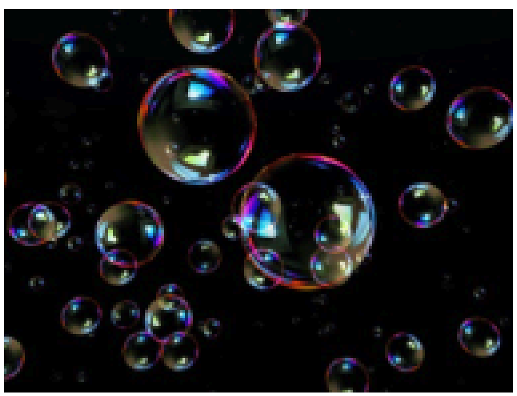
$$= (4\pi r^2 dr) \times (2\gamma/r)$$
$$= dV \times (2\gamma/r)$$

Pressure is therefore: $p = \dfrac{2\gamma}{r}.$



Pressure inside a spherical bubble?



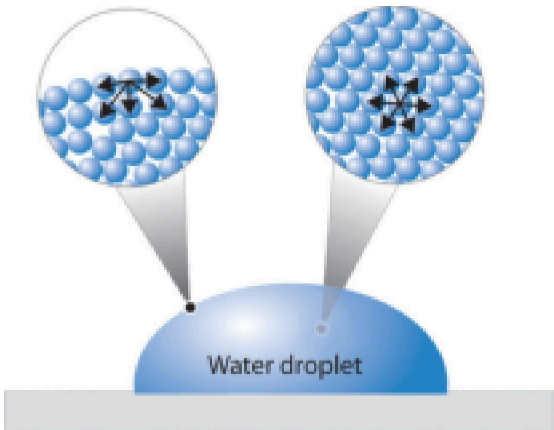


A bubble has two surfaces. The pressure of gas inside the bubble minus the pressure outside the bubble has to support two surfaces.

If the two surfaces have the same radius (thin wall), then:

$$p_{\text{bubble}} - p_0 = \frac{4\gamma}{r}$$

Microscopic origin of surface tension



https://chem.libretexts.org/@api/deki/files/128289/clipboard_ec0f0ded0ebd2efc9b1c0709dde67efab.png?revision=1

A molecule in the bulk of the liquid is attracted to its nearest neighbors by intermolecular forces (which is what holds a liquid together), and these forces are applied to a given molecule by its neighbors from all directions.

The molecules at the surface are only attracted by their neighboring molecules in one directionmbut there is no corresponding attractive force out into the bulk.

The surface has a higher energy than the bulk because bonds have to be broken in order to make a surface, and γ indicates how much energy you need to form a unit area of surface

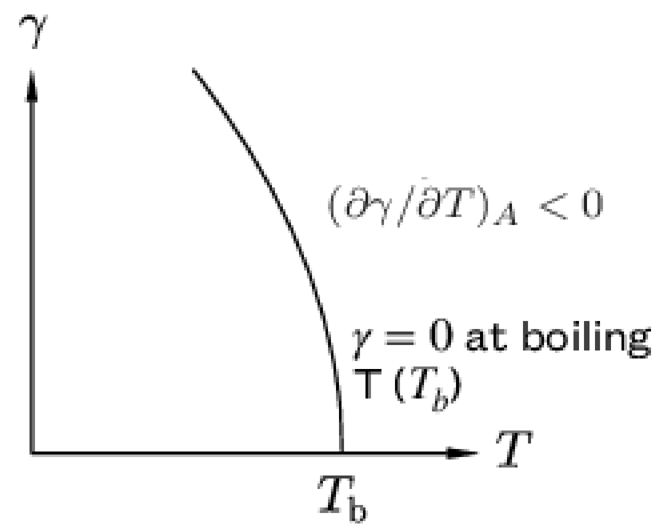
Let's do some thermodynamics

Internal energy: $\mathrm{d}U = T\,\mathrm{d}S + \gamma\,\mathrm{d}A$

Helmholtz free energy: $\mathrm{d}F = -S\,\mathrm{d}T + \gamma\,\mathrm{d}A$

Maxwell's relation: $\left(\frac{\partial S}{\partial A}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_A$

$$\left(\frac{\partial U}{\partial A}\right)_T = T\left(\frac{\partial S}{\partial A}\right)_T + \gamma \quad \Longrightarrow \quad \left(\frac{\partial U}{\partial A}\right)_T = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_A$$

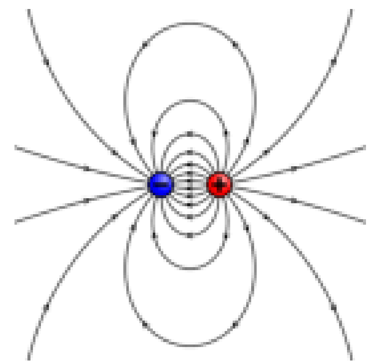


Electric and Magnetic dipoles

Interaction between electric dipole moment and electric field: $-\boldsymbol{p}_{\mathrm{E}} \cdot \boldsymbol{E}$

If the electric field changes: $\mathrm{d}(-\boldsymbol{p}_{\mathrm{E}} \cdot \boldsymbol{E}) = -\boldsymbol{p}_{\mathrm{E}} \cdot \mathrm{d}\boldsymbol{E} - \boldsymbol{E} \cdot \mathrm{d}\boldsymbol{p}_{\mathrm{E}}.$

Energy stored in the dipole itself changes when separation changes: $\mathrm{d}p_{\mathrm{E}} = q\,\mathrm{d}a$



Wikipedia

Work done to change length a is thus: $E(q\,\mathrm{d}a) = E\,\mathrm{d}p_{\mathrm{E}}$

Total work: $đW = -\boldsymbol{p}_{\mathrm{E}} \cdot \mathrm{d}\boldsymbol{E}$

Analogously: $đW = -\boldsymbol{m} \cdot \mathrm{d}\boldsymbol{B}$

Note: the system here is both the dipole and the field!

Paramagnetism

Consider a system of magnetic moments on a lattice at temperature T.

The moments do not interact with each other $\mathrm{d}U = T\,\mathrm{d}S - m\,\mathrm{d}B$

Paramagnetism: moments m all align when a magnetic field B is applied

Magnetic moment $m = MV$ with **magnetization** M and volume V

Magnetic susceptibility: $\chi = \lim_{H\to 0} \frac{M}{H}$

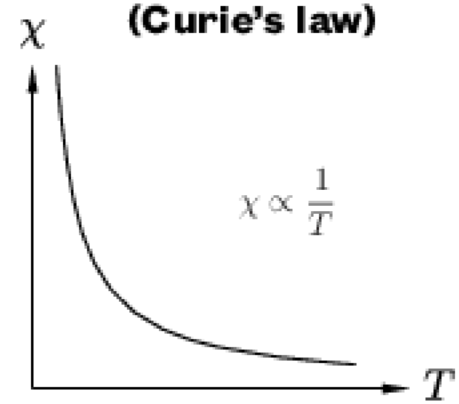
For most paramagnets $\chi \ll 1$ so that

and hence

Temperature dependence (Curie's law): $\chi \propto \frac{1}{T}$

And we have: $\left(\frac{\partial \chi}{\partial T}\right)_B < 0$

Magnetic susceptibility (Curie's law)



Isothermal magnetization

Heat emitted during isothermal increase in B

Adiabatic demagnetization

Temperature is reduced for an adiabatic reduction in B

Helmholtz free energy: $\mathrm{d}F = -S\,\mathrm{d}T - m\,\mathrm{d}B$

Maxwell's relation: $\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B \approx \frac{VB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B$ "isothermal change in entropy when changing B"

Heat "absorbed" during the isotherm: $\Delta Q = T\left(\frac{\partial S}{\partial B}\right)_T \Delta B = \frac{TVB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B \Delta B < 0$ <0 means emitted

Temperature change during an adiabatic change of B: $\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_B \left(\frac{\partial S}{\partial B}\right)_T$

Heat capacity at constant B: $C_B = T\left(\frac{\partial S}{\partial T}\right)_B$

And we find: $\left(\frac{\partial T}{\partial B}\right)_S = -\frac{TVB}{\mu_0 C_B}\left(\frac{\partial \chi}{\partial T}\right)_B$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1,$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

This number is positive, meaning we can cool a material using an adiabatic demagnetization

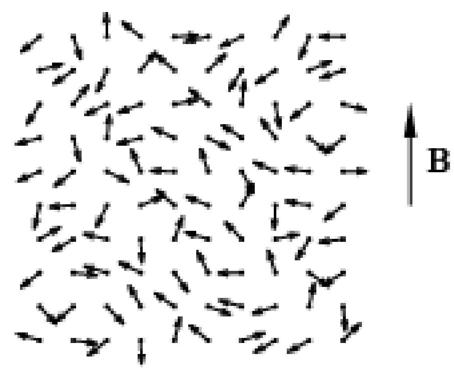
This is a way to get to very small temperatures!

Microscopic point of view

N independent moments.
They are initially randomly oriented → no net magnetization

A B will tend to align the moments but higher T will reduce magnetization

At large T, we have a random distribution, k_bT is large and all states are occupied with equal probability, regardless of their energy



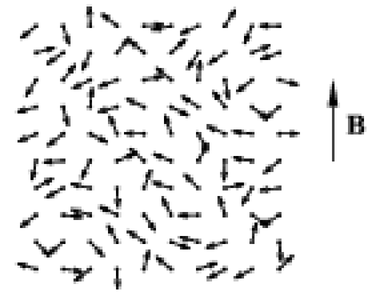
(a) high temperature

Microscopic point of view (2)

Imagine spin 1/2 systems, with only two possible orientations

Number of microstates: $\Omega = 2^N$

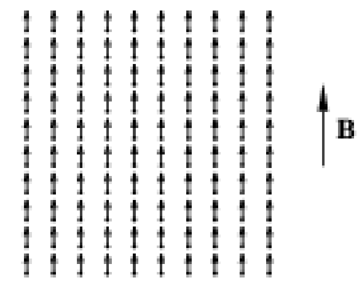
The entropy associated with the magnetic ordering is $S = k_B \ln \Omega = N k_B \ln 2$



(a) high temperature

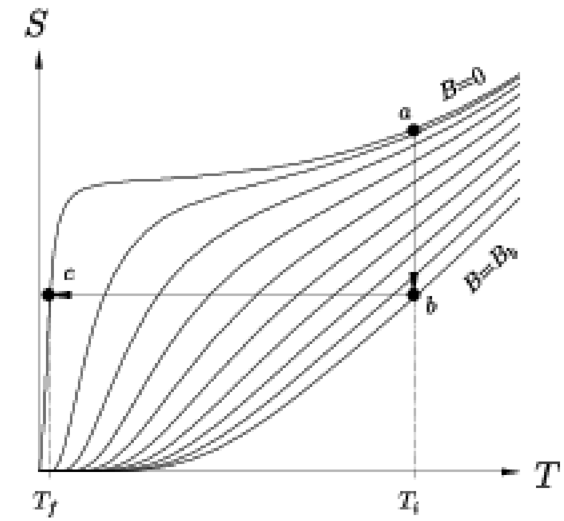
At low T, the entropy of the paramagnetic salt must reduce as only the lowest energy levels are occupied (better alignment)

At very low T, all the magnetic moments will align with the magnetic field to minimize their energy. In this case there is only one way of arranging the system (with all spins aligned) so $\Omega = 1$and $S = 0$



(b) low temperature

Magnetic Cooling: 2 steps



a to b: isothermal magnetization

Reduction of the energy of the system by aligning moments, increasing the strength of the magnetic field (bath of He at 4.2K, which absorbs the heat and the system's entropy decreases). This is done with an exchange gas.

b to c: adiabatic demagnetization

Pump away exchange gas (remove bath); magnetic field is slowly reduced to zero; processes is reversible and thus entropy is constant. The temperature is reduced

The entropy of the sample remains constant while the entropy of the magnetic moments increases (random orientations) which is counterbalanced by entropy of phonons (vibrations) [exchange of entropy between spin and phonons]

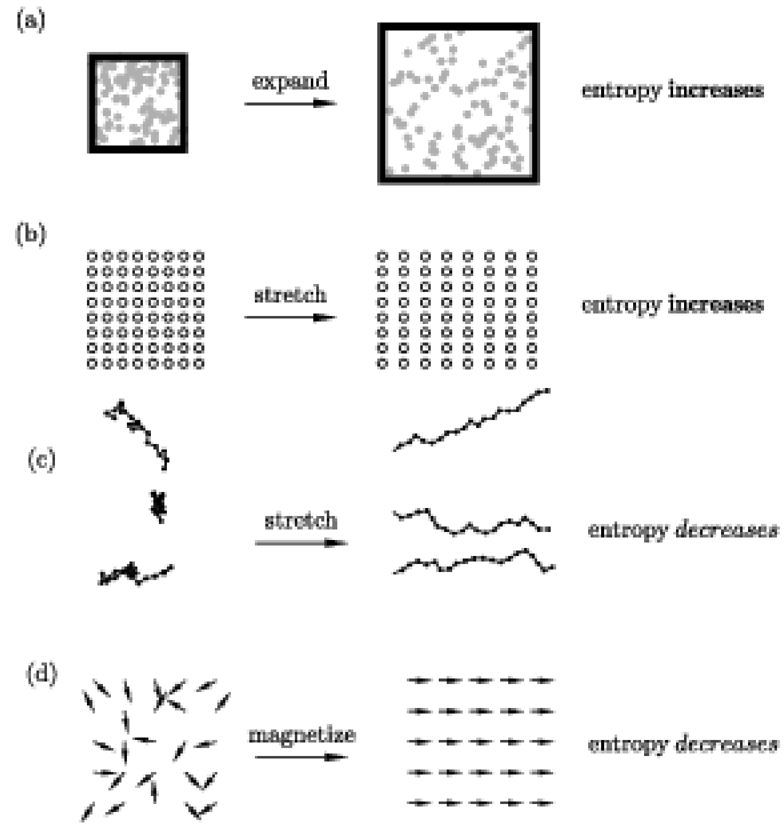
Summary

(a) The first law for a gas is $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$. An isothermal expansion results in S increasing. An adiabatic compression results in T increasing.

(b) The first law for an elastic rod is $\mathrm{d}U = T\mathrm{d}S + f\mathrm{d}L$. An isothermal extension of a metal wire results in S increasing but for rubber S decreases. An adiabatic contraction of a metal wire results in T increasing (but for rubber T decreases

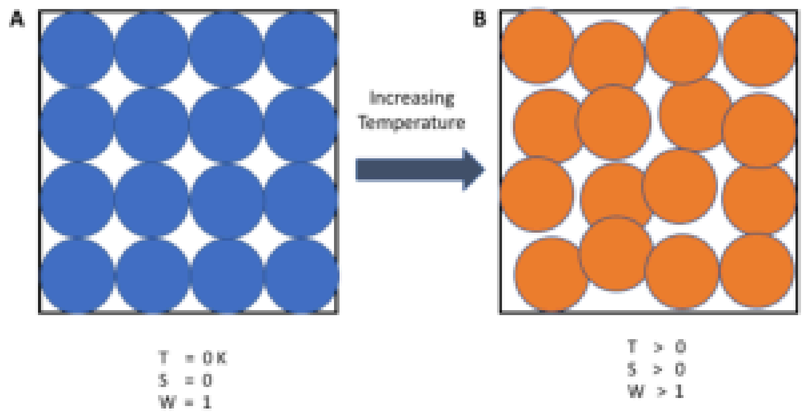
(c) The first law for a liquid surface is $\mathrm{d}U = T\mathrm{d}S + \gamma \mathrm{d}A$. An isothermal stretching results in S increasing. An adiabatic contraction results in T increasing.

(d) The first law is $\mathrm{d}U = T\mathrm{d}S - m\mathrm{d}B$ for a magnetic system. An isothermal magnetization results in S decreasing. An adiabatic demagnetization results in T decreasing.



Lecture 18. *Third Law*

- More about Entropy
- Absolute value of entropy?
- How can we measure entropy?



Wikipedia