Thermodynamics lecture 7.

W.A.L.T.

1. Natural variables

Applications of thermodynamic reasoning to:

2. Rod and rubber band
3. Surface tension 1: pressure in a water drop
4. Surface tension 2: properties of the surface
5. Paramagnet and adiabatic demagnetization

Function	Significance	Natural variables	Maxwell relation
U	Energy content	S, V, N	$\left.\frac{\partial T}{\partial V}\right\|_S = -\left.\frac{\partial p}{\partial S}\right\|_V$
F	Effective potential energy for system at fixed T	T, V, N	$\left.\frac{\partial S}{\partial V}\right\|_T = \left.\frac{\partial p}{\partial T}\right\|_V$
H	Related to energy changes at fixed pressure $\Delta H =$ process energy, latent heat, heat of reaction	S, p, N	$\left.\frac{\partial T}{\partial p}\right\|_S = \left.\frac{\partial V}{\partial S}\right\|_p$
G	Determines direction of phase and chemical changes	T, p, N	$-\left.\frac{\partial S}{\partial p}\right\|_T = \left.\frac{\partial V}{\partial T}\right\|_p$
Ω	Useful in general study of open systems	T, V, μ	

A thermodynamic potential expressed as a function of its natural variables

$$F(T, V, N) = \frac{N k_B T}{\gamma - 1}\left(1 - \ln \frac{k_B T}{\gamma - 1}\right) - N k_B T \ln a \frac{V}{N}.$$

where a and γ are constants.

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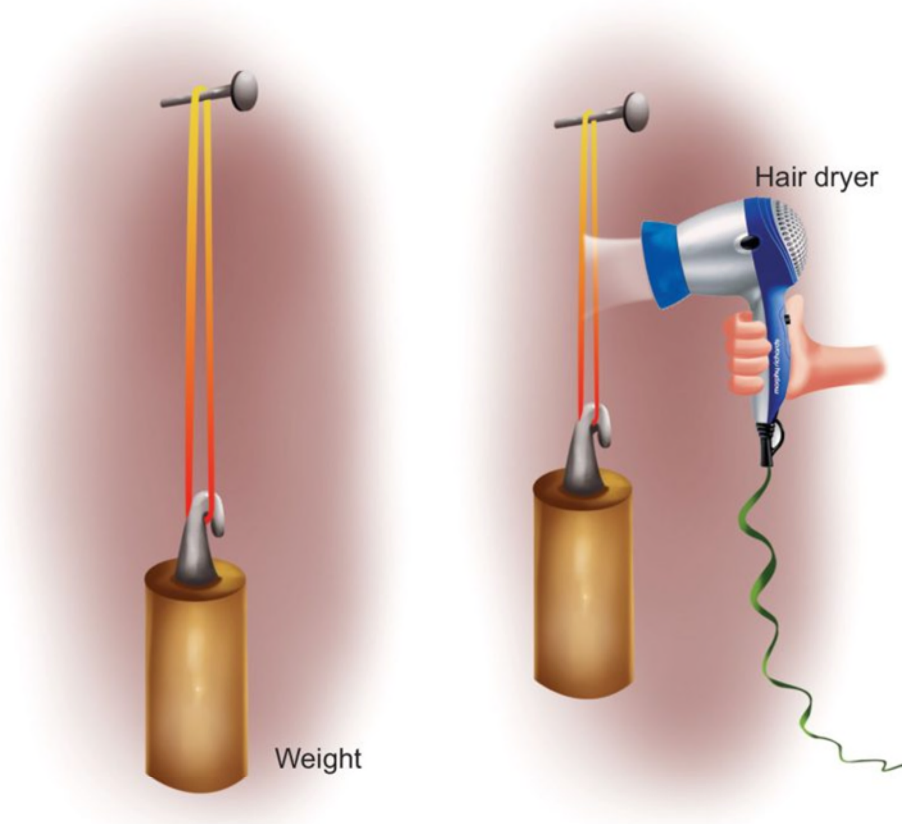
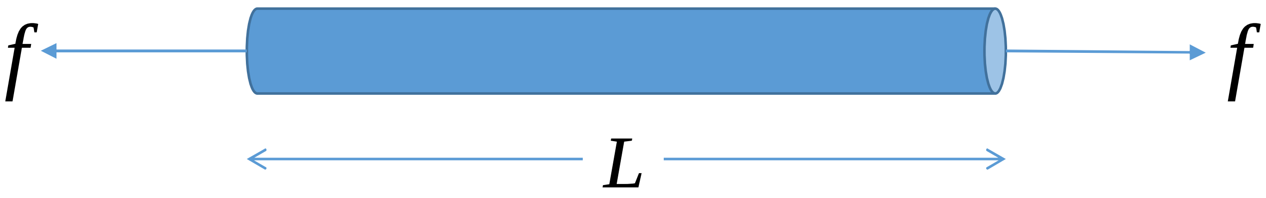
If you heat the strings of a guitar the tension goes **down**

(so the instrument goes flat)



If you heat a rubber band in ordinary conditions then the tension goes **up**: it pulls harder at any given length.

Rod or wire in tension



$$\mathrm{d}U = T\mathrm{d}S + f\mathrm{d}L$$

$$E_T = \frac{L}{A}\left.\frac{\partial f}{\partial L}\right|_T$$

Isothermal Young's modulus,

Must be positive for stable equilibrium

$$\alpha_f = \frac{1}{L}\left.\frac{\partial L}{\partial T}\right|_f$$

Linear expansivity at constant tension, may be +ve or –ve (“expand or shrink on heating”)

definitions

reciprocity relation gives

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

Indicates what happens to the tension as temperature is raised

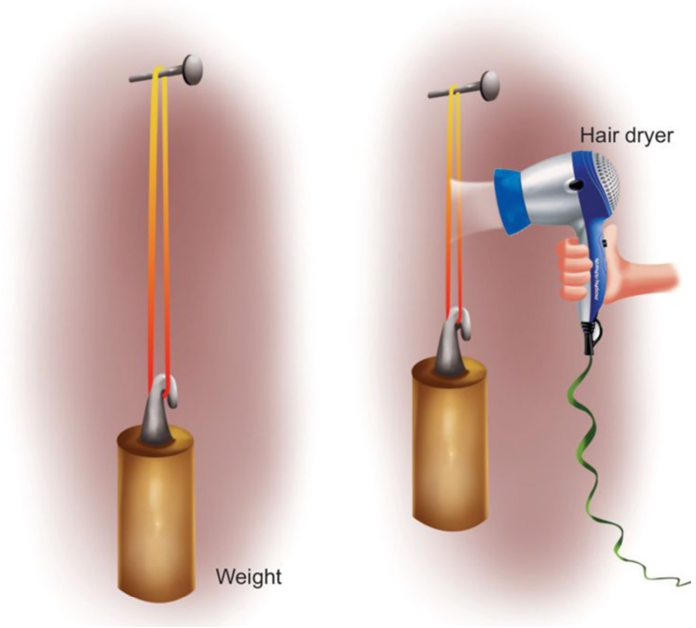
$$\left.\frac{\partial f}{\partial T}\right|_L = -\left.\frac{\partial f}{\partial L}\right|_T \left.\frac{\partial L}{\partial T}\right|_f = -AE_T\alpha_f$$

Catgut, nylon, steel:

expand on heating so alpha is POSITIVE

Hence our equation tells us that

tension goes down on heating (instrument goes flat)

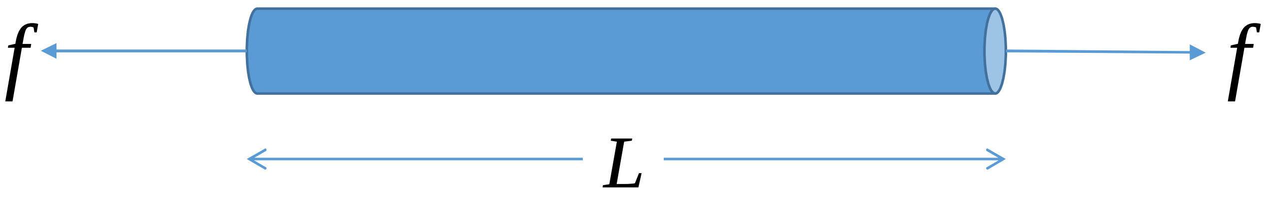


Rubber band **shrinks** on heating so alpha is NEGATIVE

Hence our equation tells us that

tension goes UP on heating (at a fixed length it will pull harder)

Now consider entropy



$$\boxed{dU = TdS + f dL}$$

We just found:

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

(reciprocity)

Maxwell relation
(from $dF = -SdT + f\,dL$)

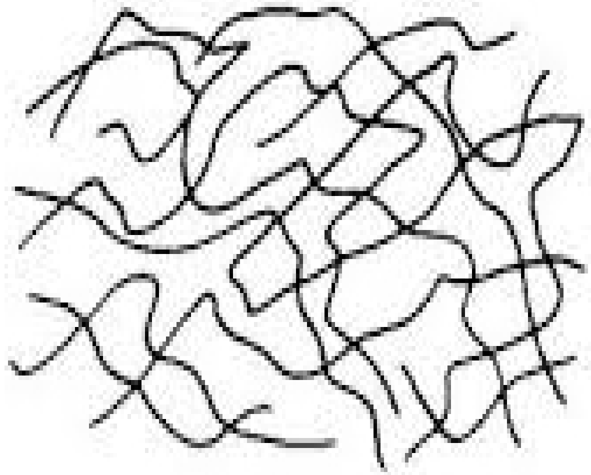
$$\left.\frac{\partial S}{\partial L}\right|_T = -\left.\frac{\partial f}{\partial T}\right|_L$$

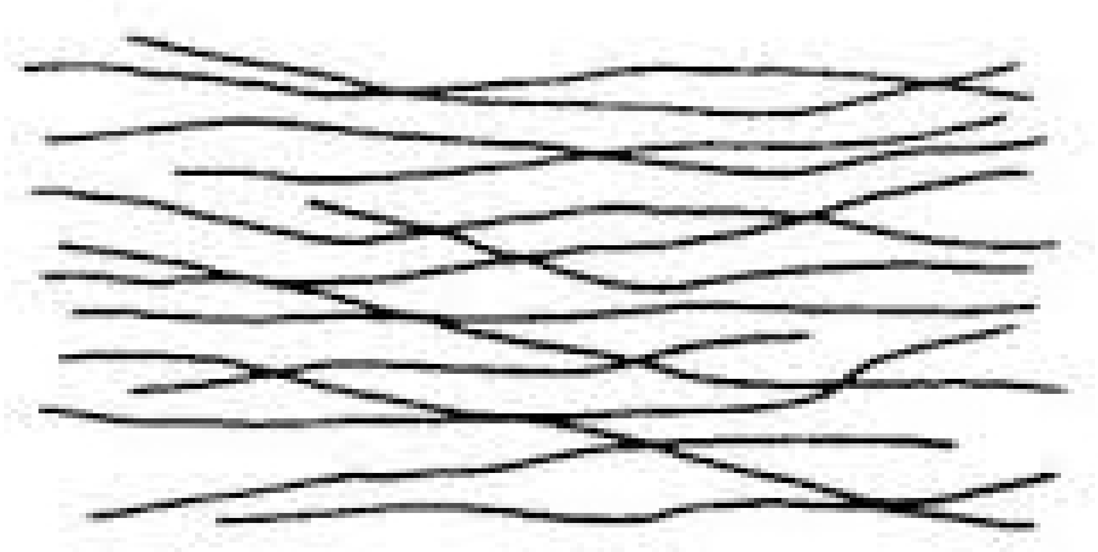
Hence

$$\boxed{\left.\frac{\partial S}{\partial L}\right|_T = AE_T\alpha_f}$$

So +ve α → S increases with L
-ve α → S decreases with L

Why does the entropy go down not up when you stretch a rubber band?





Under macroscopic constraints which fix the tension and length of the rubber band:

Case 1. Small length of rubber band
→
many different molecular shapes are possible under the macroscopic constraints
→
High entropy

Case 2. Stretch the rubber band
→
fewer different molecular shapes are possible under the macroscopic constraints
→
low entropy

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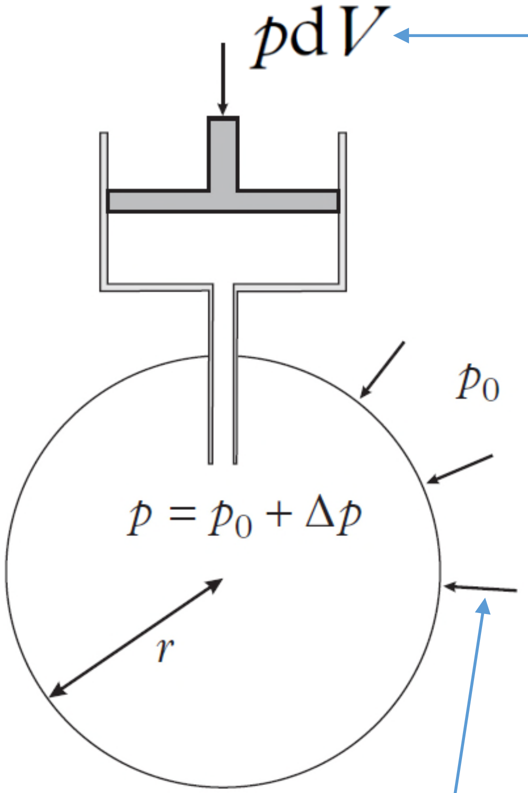
Surface tension

Work required to change the surface area A:

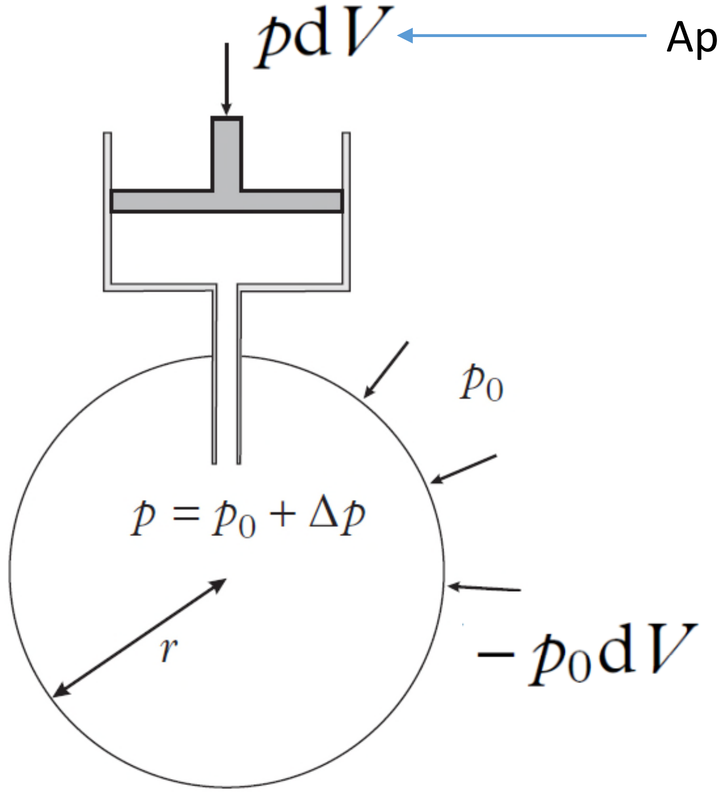
$$đW = \sigma \, \mathrm{d}A$$

Surface tension



Apply enough force here to just balance pressure in the liquid drop

The situation is balanced when the surrounding atmosphere is at a pressure less than p.



Apply enough force here to just balance pressure in the liquid drop

Energy acquired by the water when we push on the piston:

$$\text{đ}W = p\,\mathrm{d}V - p_0\,\mathrm{d}V = \sigma\,\mathrm{d}A$$

Therefore (derived on blackboard):

$$(p - p_0) = \frac{2\sigma}{r}$$

$$V = (4/3)\pi r^3$$

. . . It’s hard to blow up a small balloon

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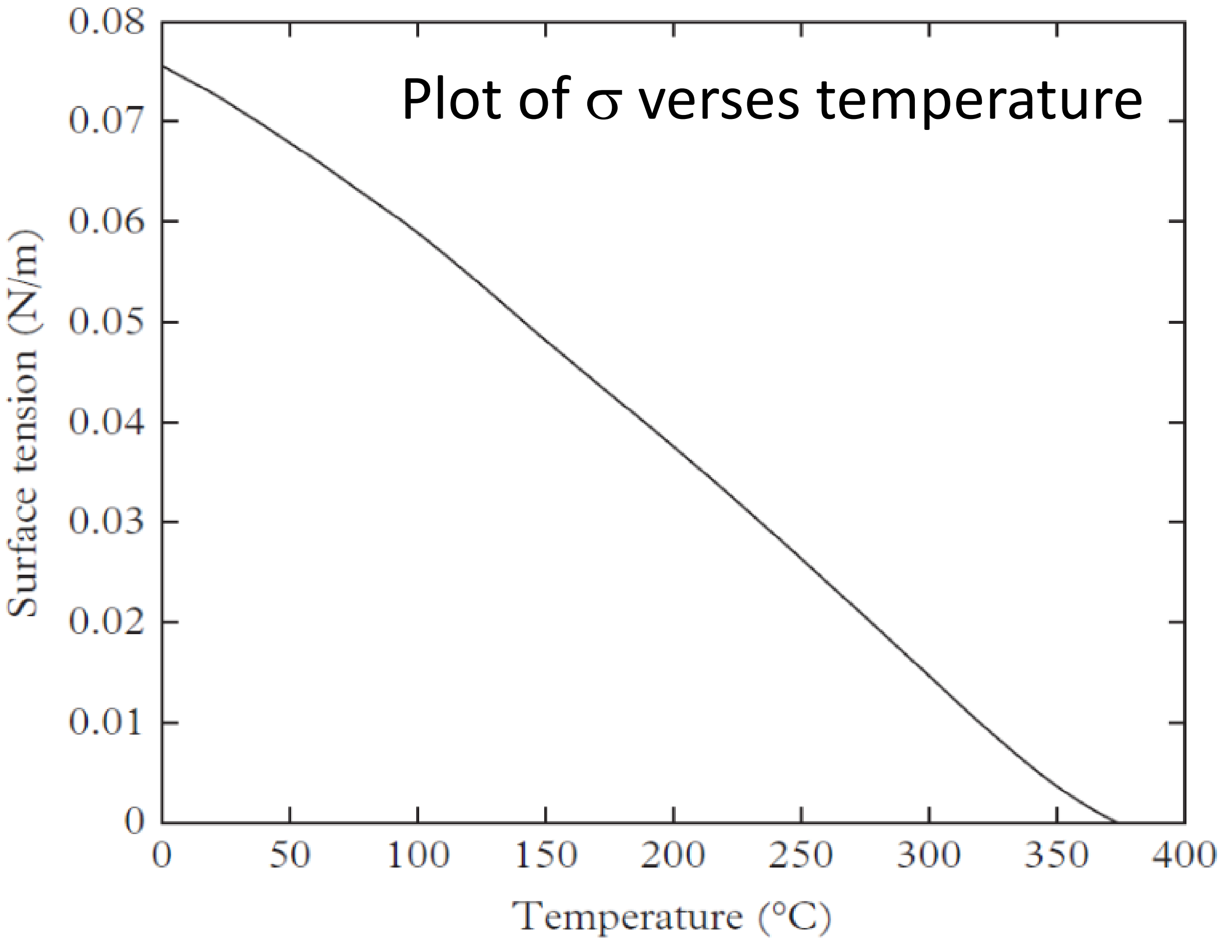
Surface tension varies with temperature



Surface tension of water in contact with air, as a function of temperature.

$$\begin{aligned} \mathrm{d}U_{\mathrm{tot}} &= \mathrm{d}U_{\mathrm{bulk}} + \mathrm{d}U_{\mathrm{surf}} \\ &= T\mathrm{d}S_{\mathrm{bulk}} - p\mathrm{d}V + \mu\mathrm{d}N + T\mathrm{d}S_{\mathrm{surf}} + \sigma\mathrm{d}A \end{aligned}$$

giving

$$\begin{aligned} \mathrm{d}U_{\mathrm{bulk}} &= T\mathrm{d}S_{\mathrm{bulk}} - p\mathrm{d}V + \mu\mathrm{d}N \\ \mathrm{d}U_{\mathrm{surf}} &= T\mathrm{d}S_{\mathrm{surf}} + \sigma\mathrm{d}A \end{aligned}$$

We can consider the surface itself as a thermodynamic system:

$$\boxed{\mathrm{d}U = T\mathrm{d}S + \sigma\,\mathrm{d}A}$$

$$\left.\frac{\partial S}{\partial A}\right|_T = -\left.\frac{\partial \sigma}{\partial T}\right|_A$$

Maxwell relation

hence

$$\left.\frac{\partial U}{\partial A}\right|_T = T\left.\frac{\partial S}{\partial A}\right|_T + \sigma = -T\left.\frac{\partial \sigma}{\partial T}\right|_A + \sigma$$

Energy stored in the surface by ripples and chemical bonds.

from *Macbeth* Act II, scene 2 (William Shakespeare)

Methought I heard a voice cry “Sleep no more!
Macbeth does murder sleep”, the innocent sleep,
Sleep that knits up the ravel’d sleeve of care,
The death of each day’s life, sore labour’s bath,
Balm of hurt minds, great nature's second course,
Chief nourisher in life’s feast,—

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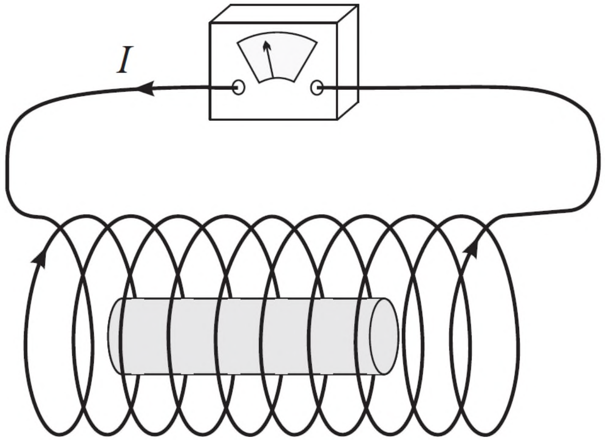
Paramagnetism



$\boldsymbol{B}$ = the field that would be present in the solenoid if the sample were removed while keeping the total flux Φ in the solenoid constant.

$$đW = -m\mathrm{d}B$$

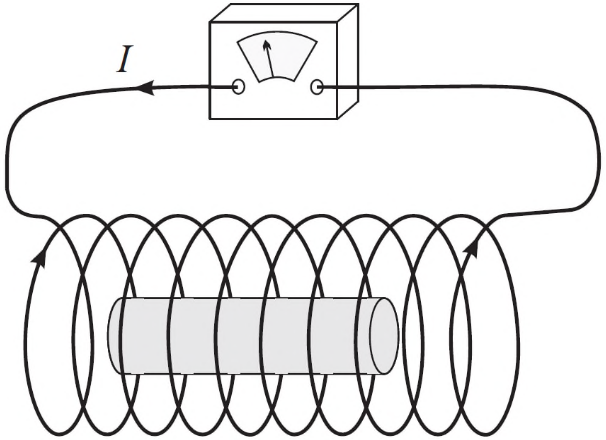
m = dipole moment = M V

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V - m\mathrm{d}B$$

neglect

$$\boxed{\mathrm{d}U = T\mathrm{d}S - m\mathrm{d}B}$$

Paramagnetism



Let’s focus on isothermal and adiabatic processes:

$$\frac{\text{đ}Q_T}{\mathrm{d}B} = T \left.\frac{\partial S}{\partial B}\right|_T$$

Heat absorbed during isothermal change

$$\left.\frac{\partial T}{\partial B}\right|_S$$

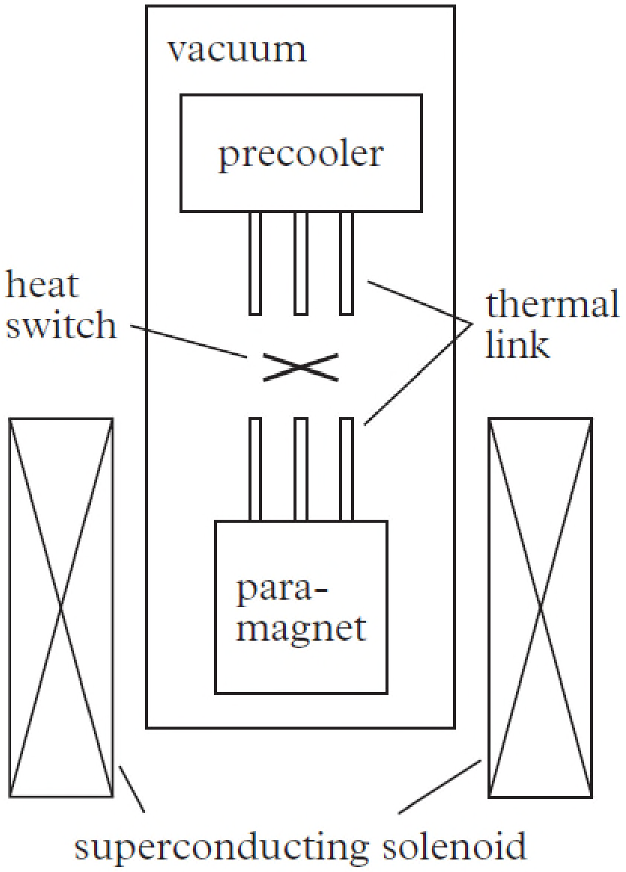
Temperature change during adiabatic process

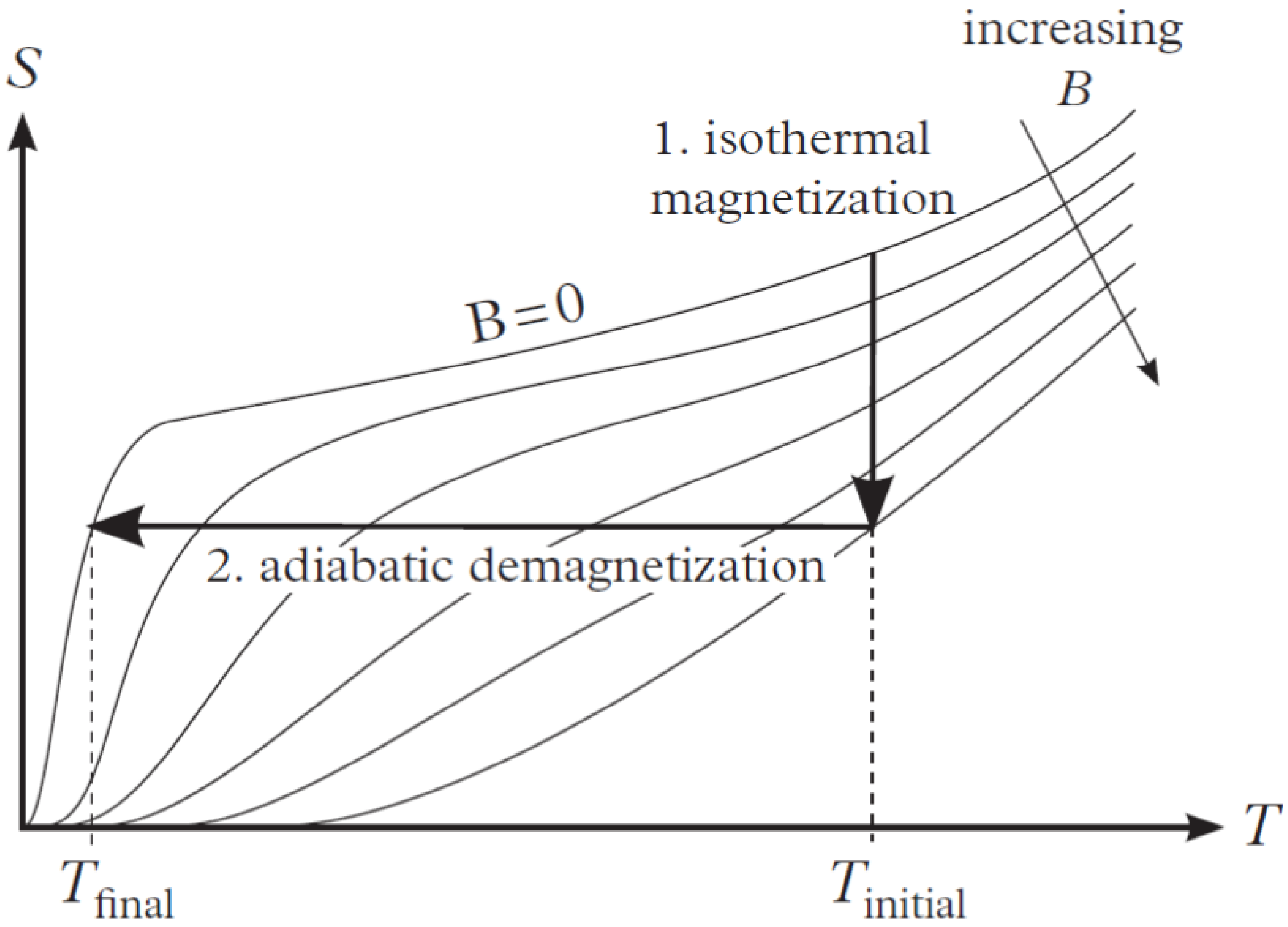
We will derive:

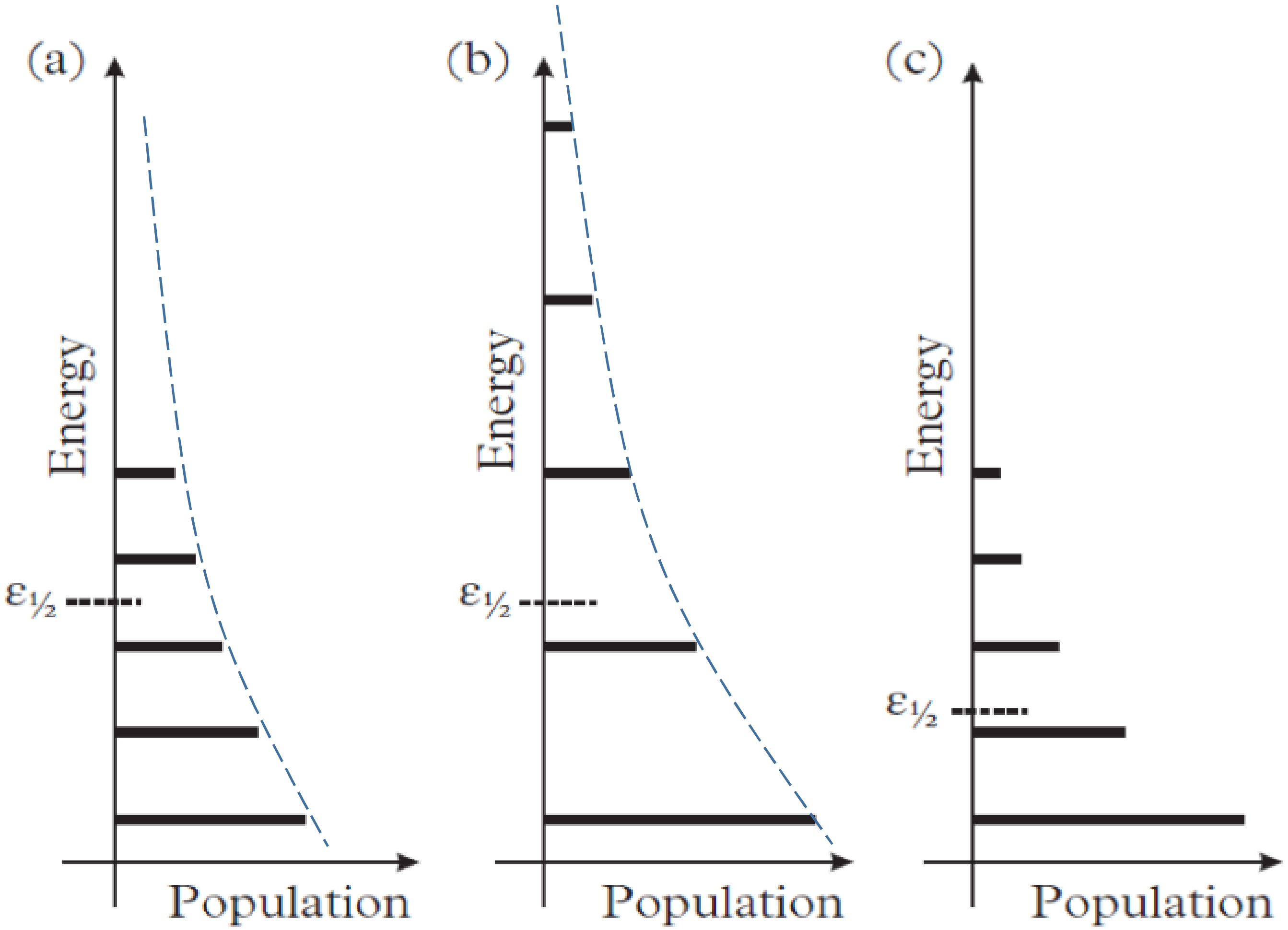
$$T \left.\frac{\partial S}{\partial B}\right|_T = \frac{TVB}{\mu_0} \left.\frac{\partial \chi}{\partial T}\right|_B$$

$$\left.\frac{\partial T}{\partial B}\right|_S = -\frac{TVB}{\mu_0 C_B} \left.\frac{\partial \chi}{\partial T}\right|_B$$

Cooling by adiabatic demagnetisation







$e^{-\frac{E}{k_B T}}$ constant in isothermal change

Isothermal
B increase

adiabatic
B decrease

Adiabatic: each population stays fixed while the energy levels move.

Examples.

1. Show that, for an elastic rod,

$$\left.\frac{\partial C_L}{\partial L}\right|_T = -T \left.\frac{\partial^2 f}{\partial T^2}\right|_L ,$$

   where C_L is the heat capacity at constant length.

2. The surface tension of liquid argon is given by $\sigma = \sigma_0(1 - T/T_c)^{1.28}$, where $\sigma_0 = 0.038$ N/m and the critical temperature $T_c = 151$ K. Find the surface entropy per unit area at the triple point, $T = 83$ K.