Thermodynamics lecture 7.

W.A.L.T.

- Natural variables

Applications of thermodynamic reasoning to:

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

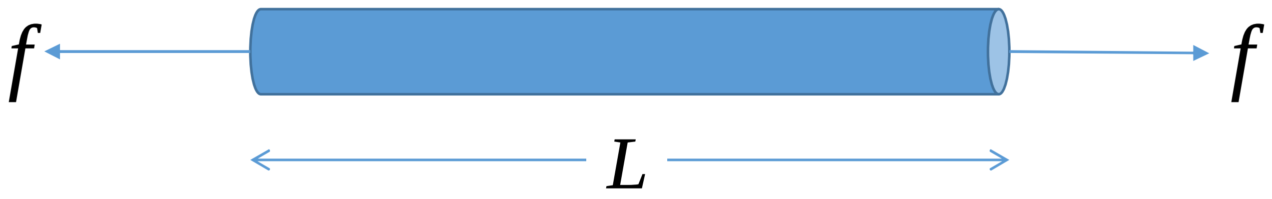
Function	Significance	Natural variables	Maxwell relation
U	Energy content	S, V, N	$\left.\frac{\partial T}{\partial V}\right\|_S = -\left.\frac{\partial p}{\partial S}\right\|_V$
F	Effective potential energy for system at fixed T	T, V, N	$\left.\frac{\partial S}{\partial V}\right\|_T = \left.\frac{\partial p}{\partial T}\right\|_V$
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.

Rod or wire in tension



$$dU = TdS + f dL$$

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

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

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

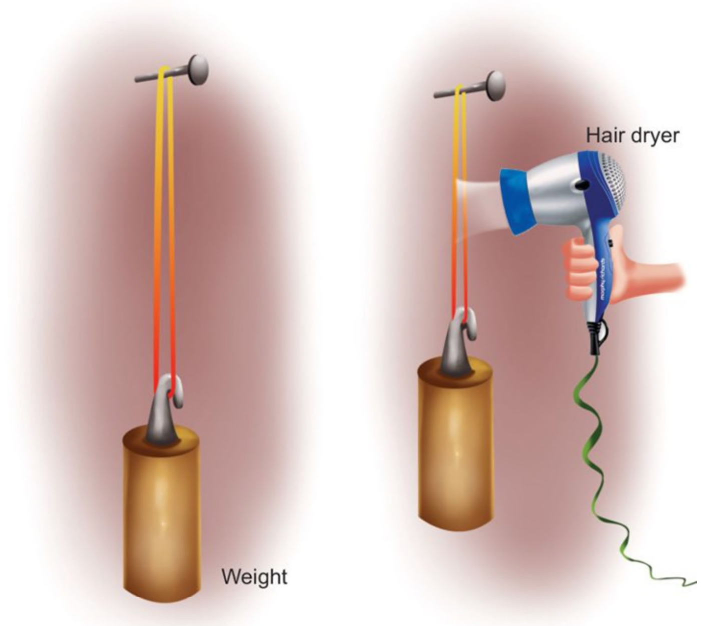
$$\left.\frac{\partial f}{\partial T}\right|_L = -\left.\frac{\partial f}{\partial L}\right|_T \left.\frac{\partial L}{\partial T}\right|_f = -AE_T\alpha_f$$

Catgut, nylon, steel:

expand on heating so alpha is POSITIVE

Hence our equation tells us that

tension goes down on heating (instrument goes flat)



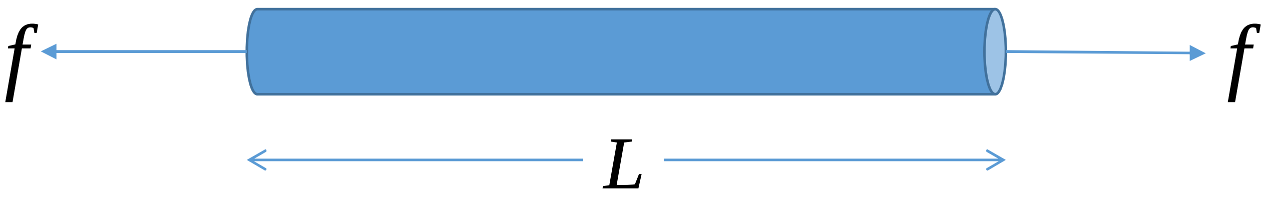
Rubber band **shrinks** on heating so alpha is NEGATIVE

Hence our equation tells us that

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

Now consider entropy

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



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Linear expansivity at constant tension, may be +ve or -ve

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(reciprocity)

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

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

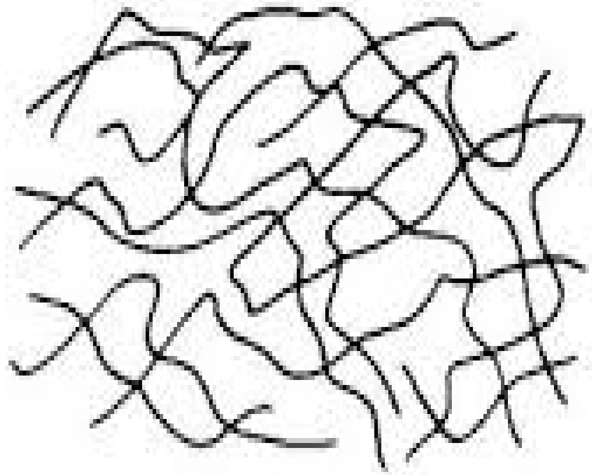
Hence

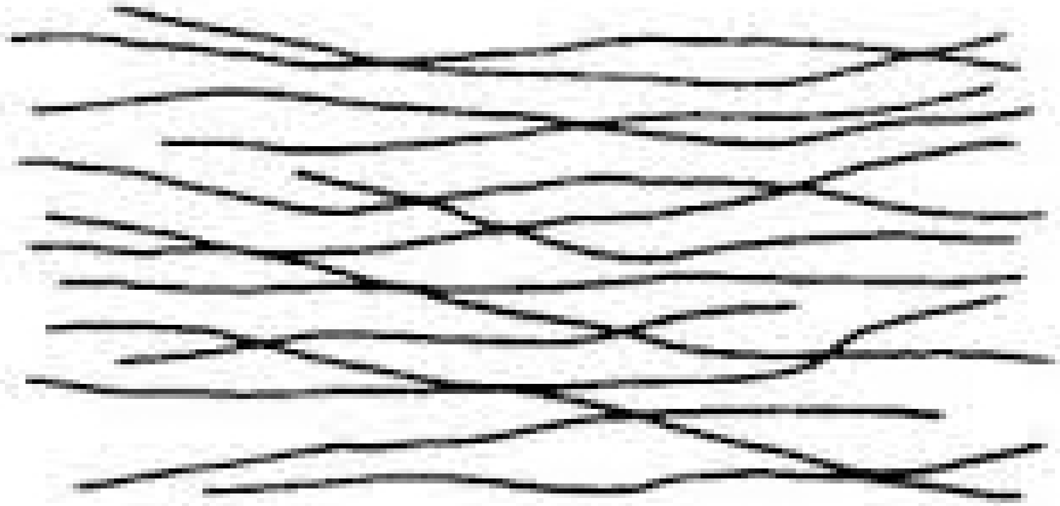
$$\left.\frac{\partial S}{\partial L}\right|_T = AE_T\alpha_f$$

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?





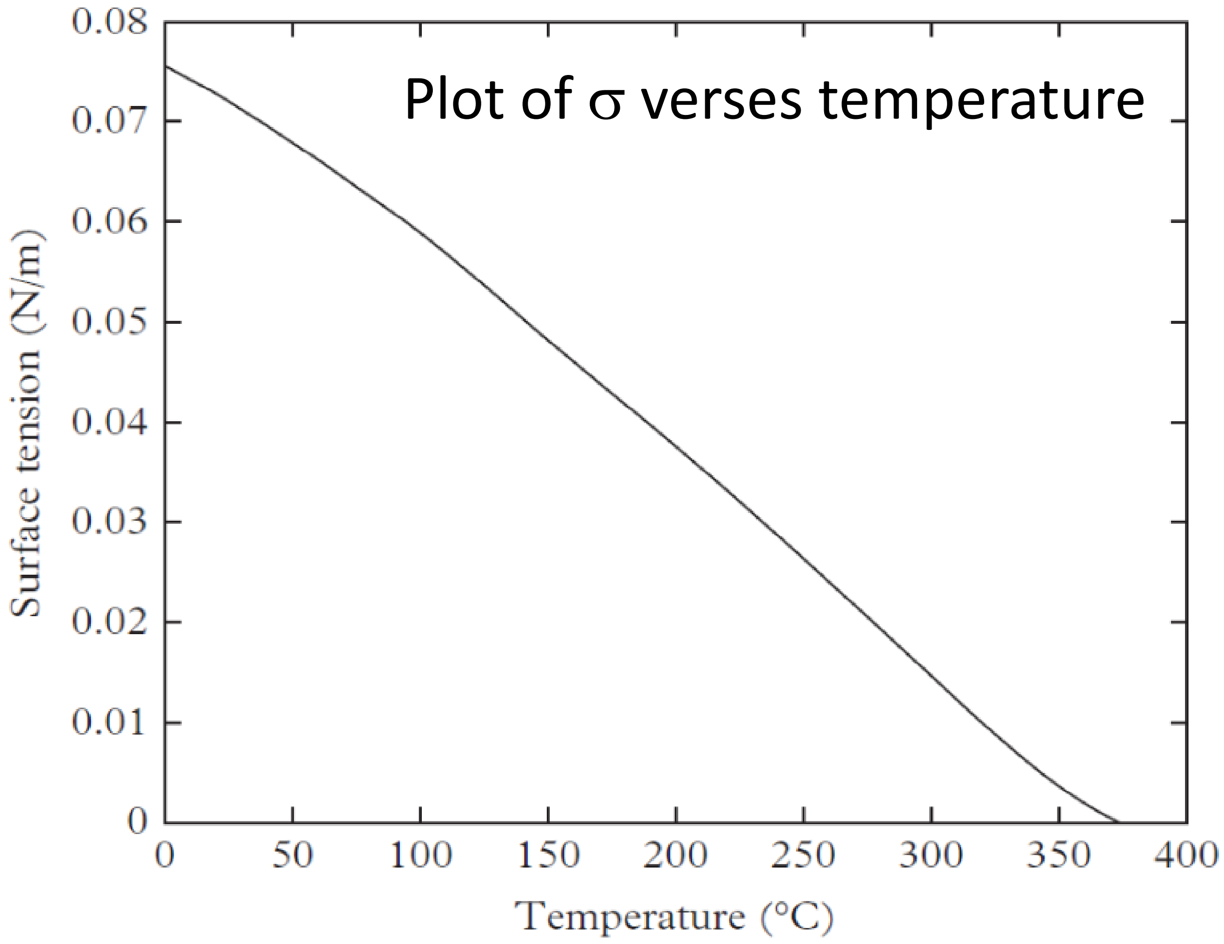
Under macroscopic constraints which fix the tension and length of the rubber band:

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

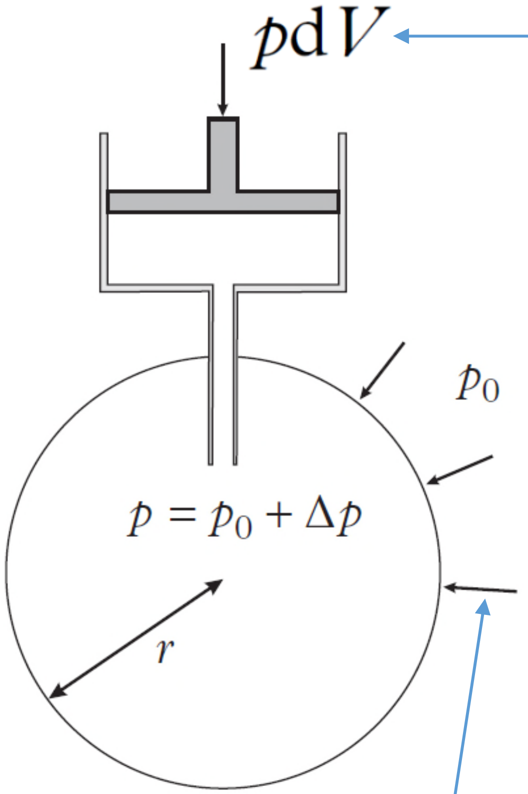
Case 2. Stretch the rubber band
→
fewer different molecular shapes are possible under the macroscopic constraints
→
low entropy

Surface tension

$$đW = \sigma \, dA$$

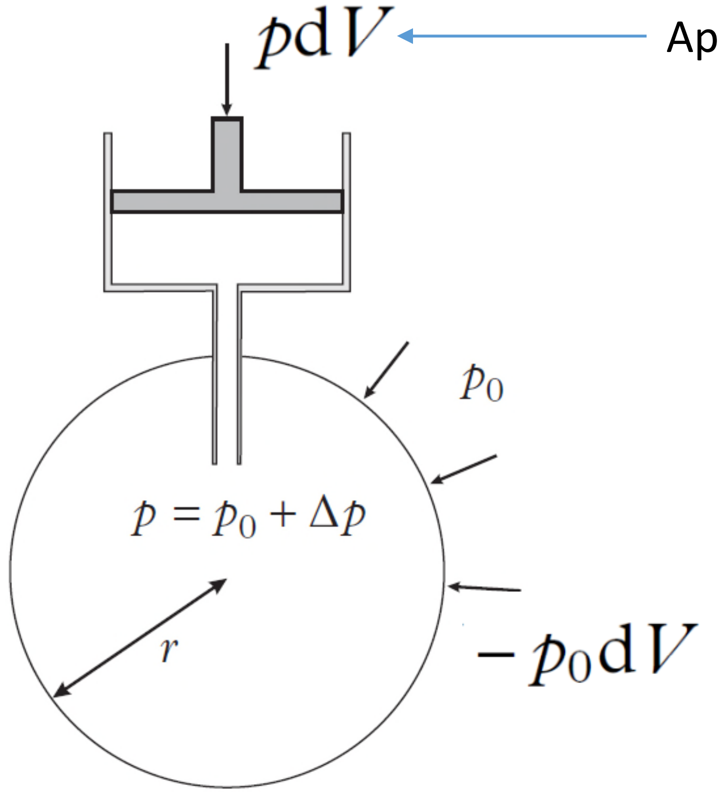


Surface tension of water in contact with air, as a function of temperature.



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

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

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

$$đW = p\,\mathrm{d}V - p_0\,\mathrm{d}V = \sigma\,\mathrm{d}A$$

Therefore (derived on blackboard):

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

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

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

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:

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

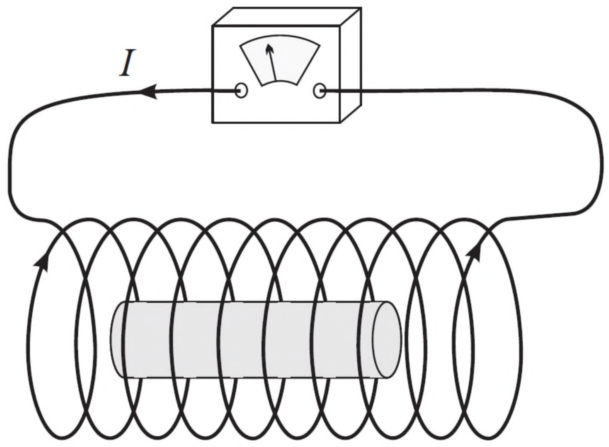
$$\left.\frac{\partial S}{\partial A}\right|_T = -\left.\frac{\partial \sigma}{\partial T}\right|_A$$

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.

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.

$$đW = -m\mathrm{d}B$$

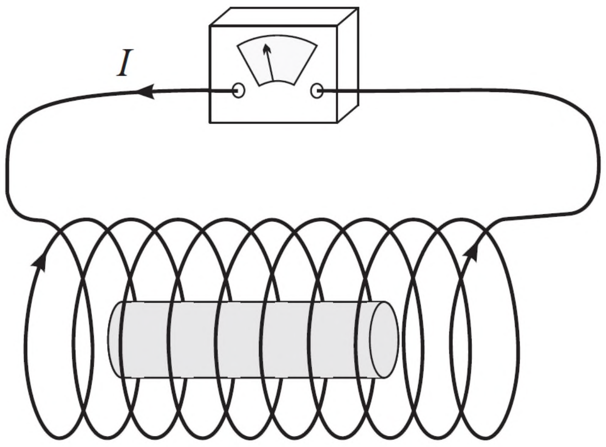
m = dipole moment = M V

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

neglect

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

Paramagnetism



Let's focus on isothermal and adiabatic processes:

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

Heat absorbed during isothermal change

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

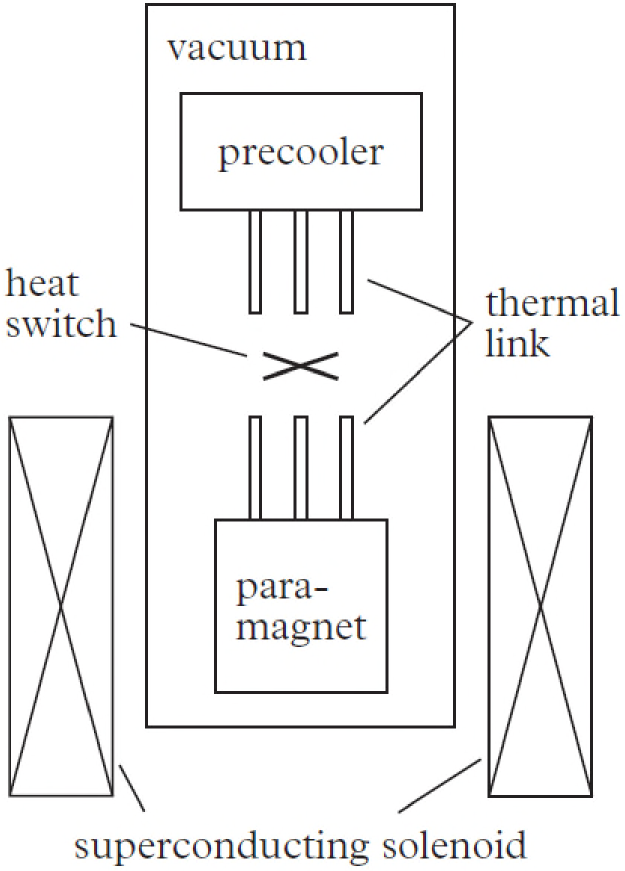
Temperature change during adiabatic process

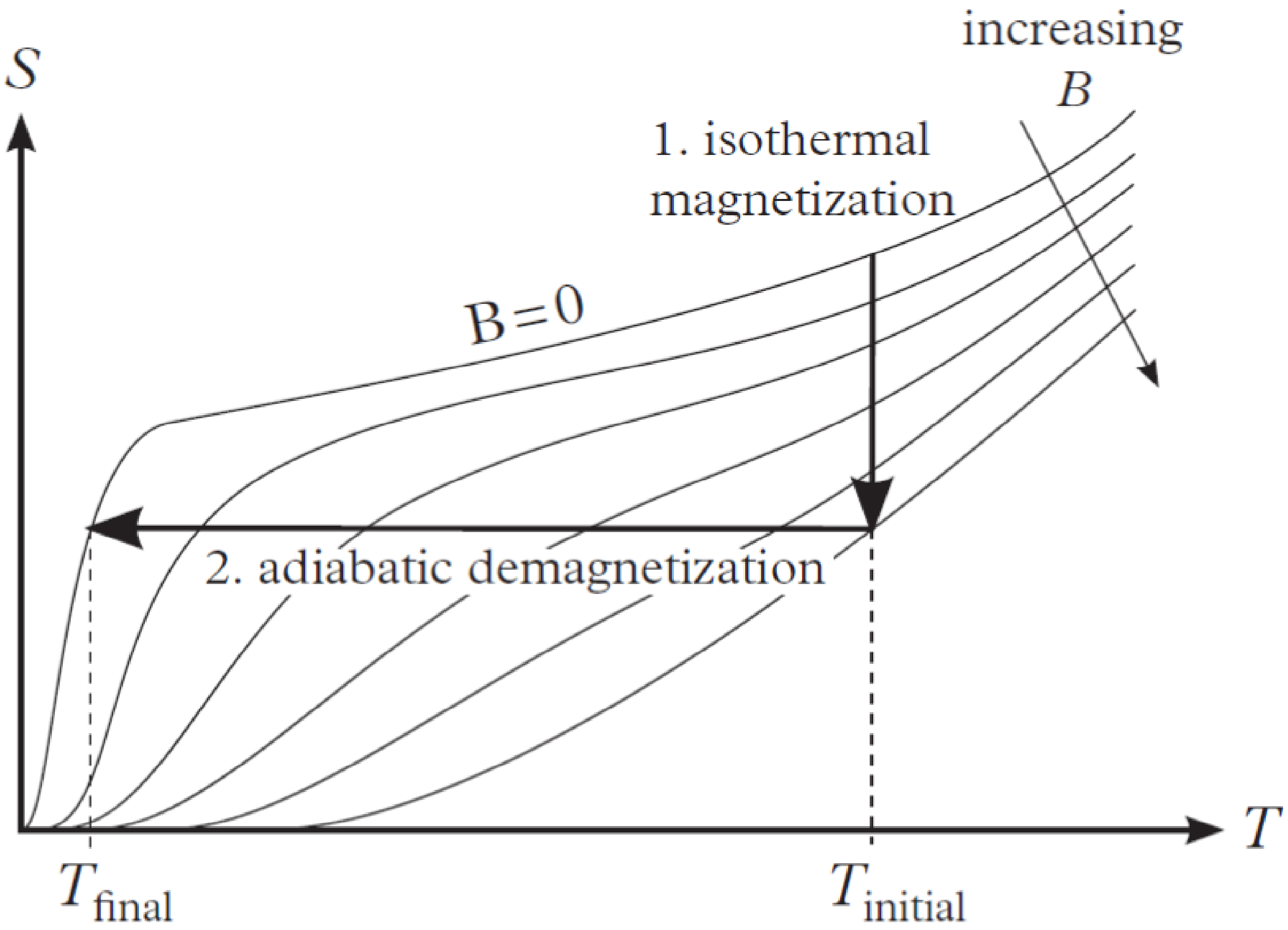
We will derive:

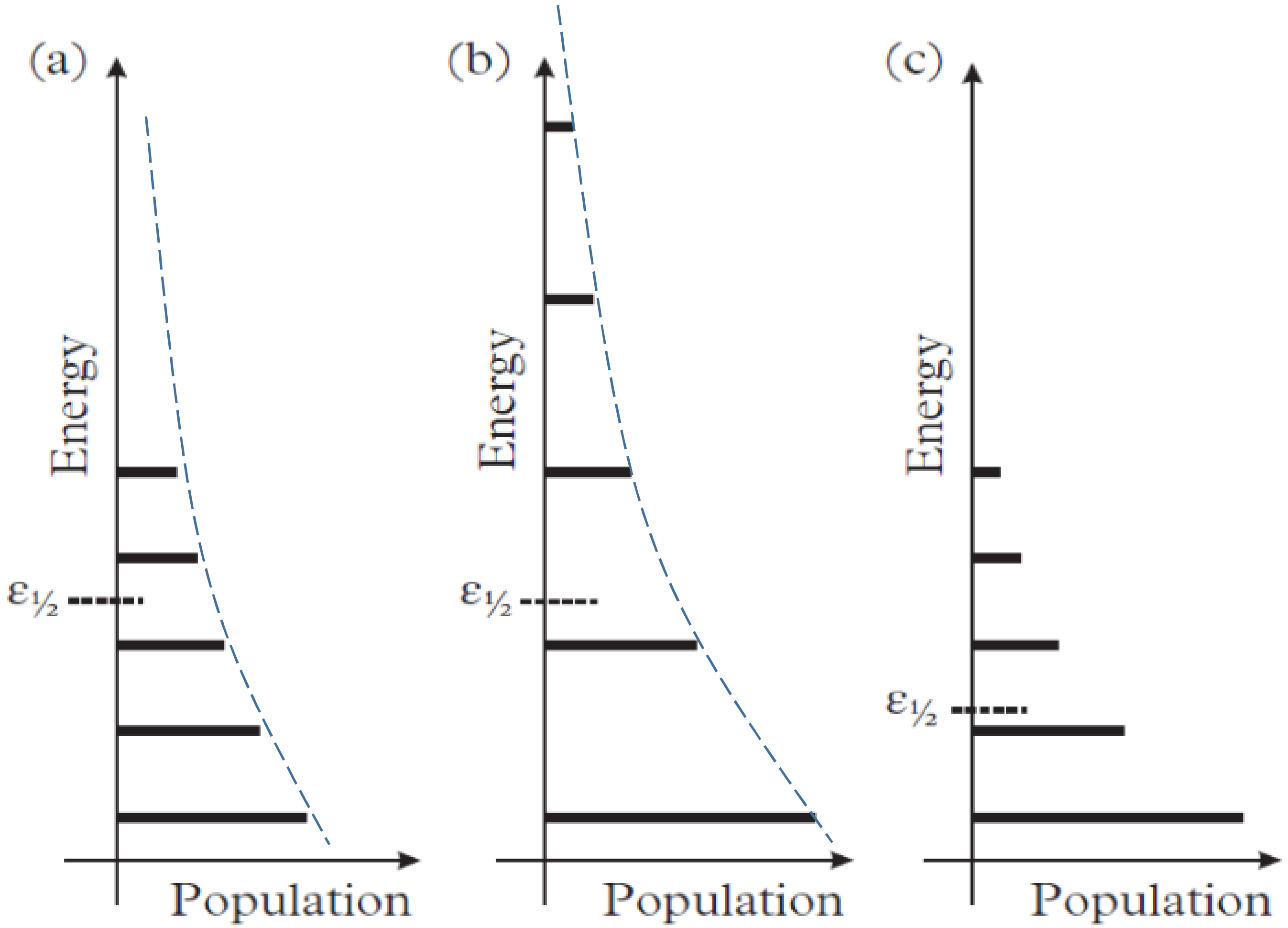
$$T \left.\frac{\partial S}{\partial B}\right|_T = \frac{TVB}{\mu_0} \left.\frac{\partial \chi}{\partial T}\right|_B$$

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

Cooling by adiabatic demagnetisation







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

Isothermal
$\boldsymbol{B}$ increase

adiabatic
$\boldsymbol{B}$ 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.