Thermodynamics lecture 7.

W.A.L.T.

- Natural variables example

Applications of thermodynamic reasoning to:

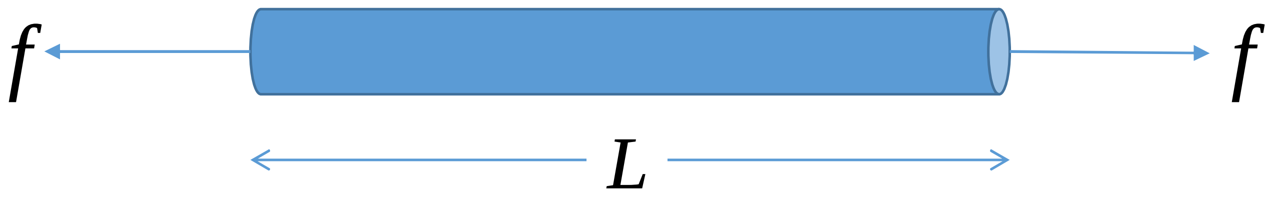
- Rod
- Surface tension
- Paramagnet and adiabatic demagnetization

A thermodynamic potential expressed as a function of its natural variables

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

where a and γ are constants.

Rod or wire in tension



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

$$E_T = \frac{L}{A}\frac{\partial f}{\partial L}\bigg|_T$$

Isothermal Young's modulus,

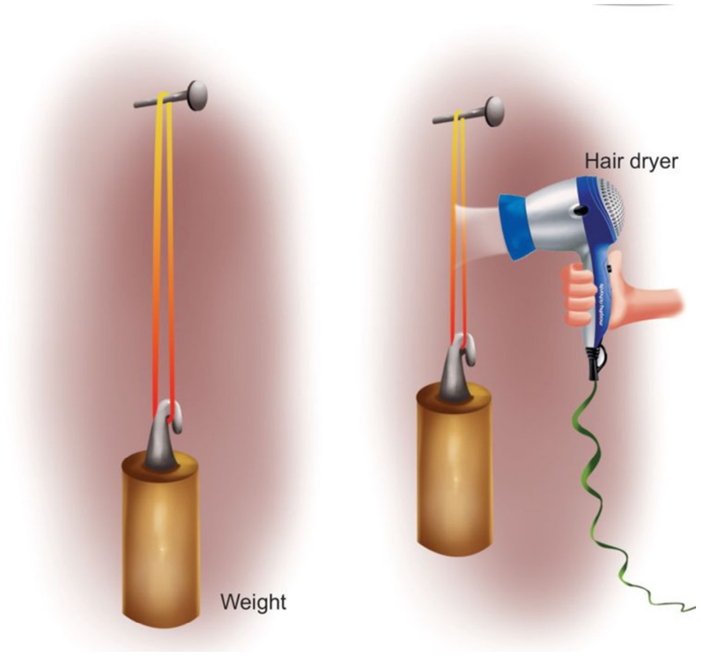
Must be positive (for stable equilibrium)

$$\alpha_f = \frac{1}{L}\frac{\partial L}{\partial T}\bigg|_f$$

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

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

(reciprocity)



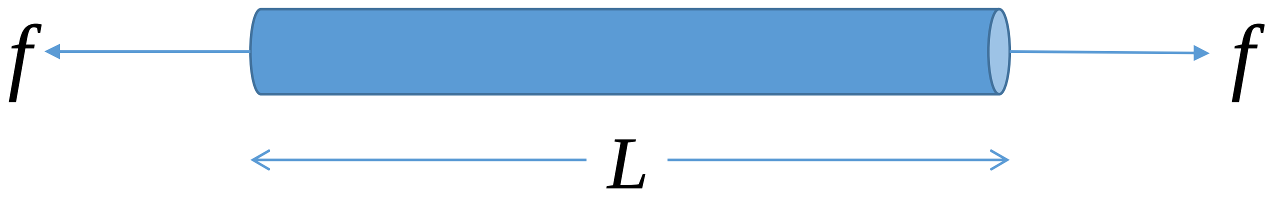
Rubber band shrinks on heating

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

- Warm violin: tension goes down (for string of fixed length)
- Warm elastic band: tension goes up

Rod or wire in tension

$$dU = T\,dS + f\,dL$$



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

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(reciprocity)

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

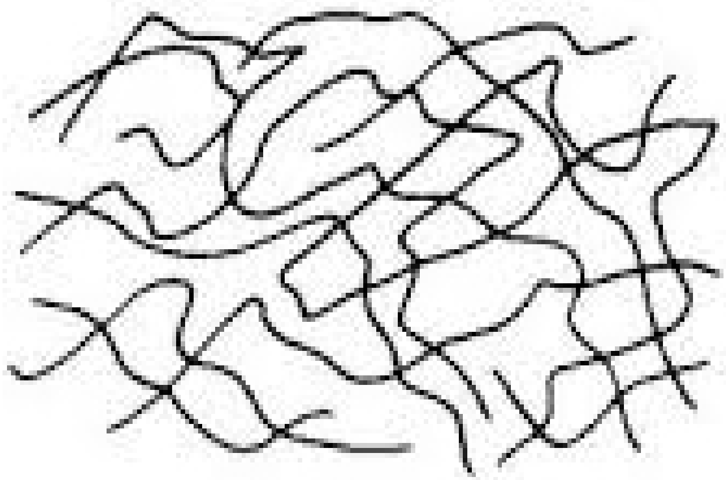
$$\left.\frac{\partial S}{\partial L}\right|_T = -\left.\frac{\partial f}{\partial T}\right|_L$$

Hence

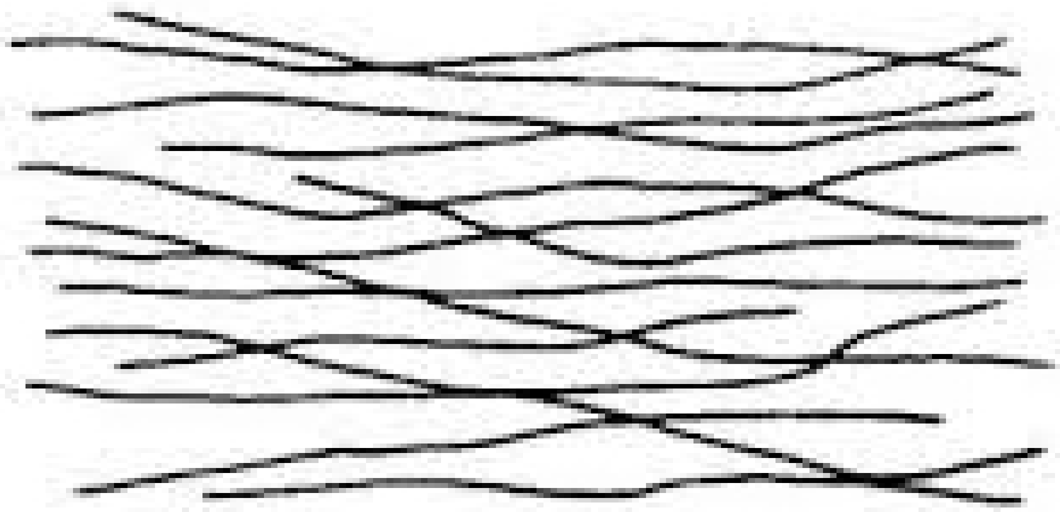
$$\left.\frac{\partial S}{\partial L}\right|_T = AE_T\alpha_f$$

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?



more different molecular shapes
are consistent with the macroscopic constraints
(the given tension and length of the material overall)
→
High entropy



fewer different molecular shapes
are consistent with the macroscopic constraints
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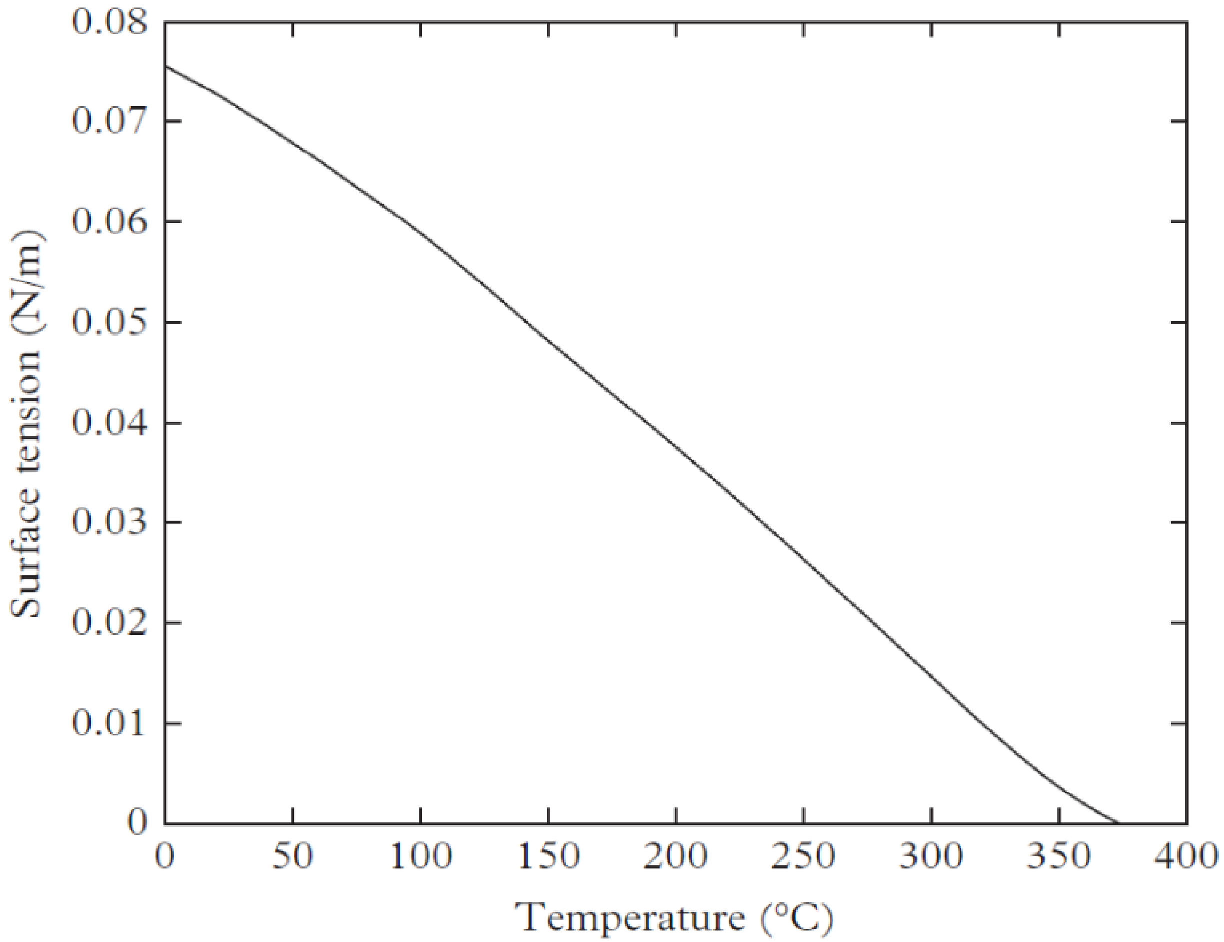
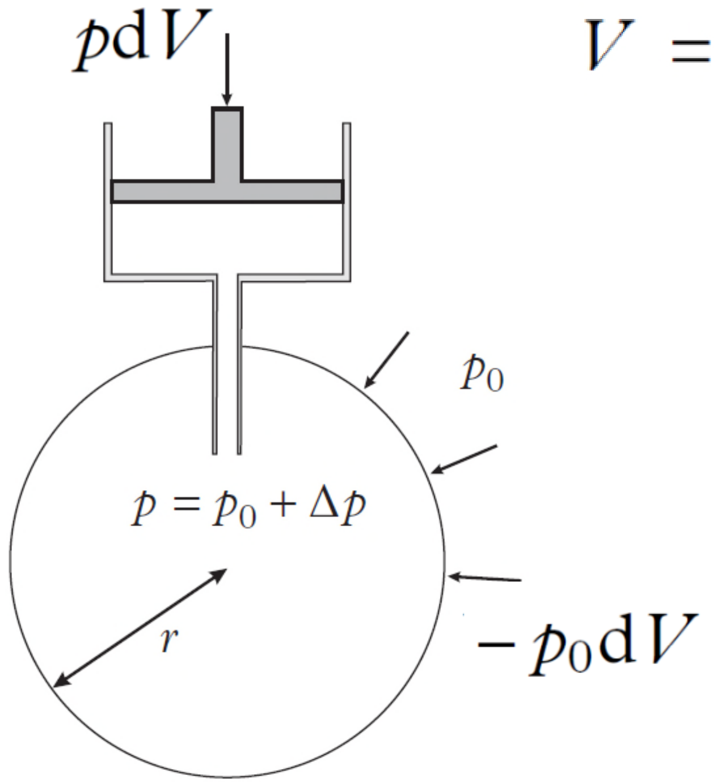
→
low entropy

Surface tension

$$đW = \sigma \, dA$$



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



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

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

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

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

$$\begin{aligned} dU_{\text{tot}} &= dU_{\text{bulk}} + dU_{\text{surf}} \\ &= TdS_{\text{bulk}} - pdV + \mu dN + TdS_{\text{surf}} + \sigma dA \end{aligned}$$

giving

$$\begin{aligned} dU_{\text{bulk}} &= TdS_{\text{bulk}} - pdV + \mu dN \\ dU_{\text{surf}} &= TdS_{\text{surf}} + \sigma dA \end{aligned}$$

We can consider the surface itself as a thermodynamic system:

$$dU = TdS + \sigma dA$$

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

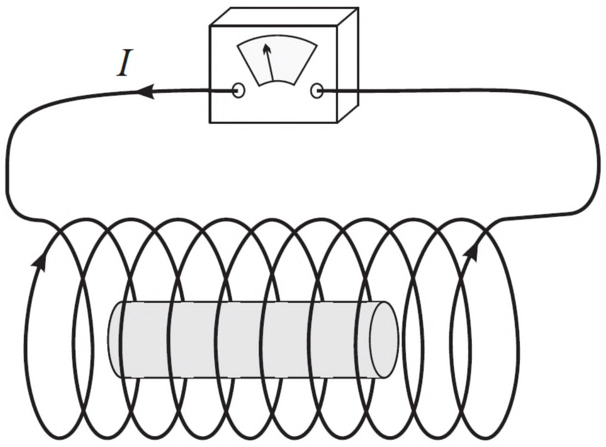
Maxwell relation

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



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.

$$đW = -m\mathrm{d}B$$

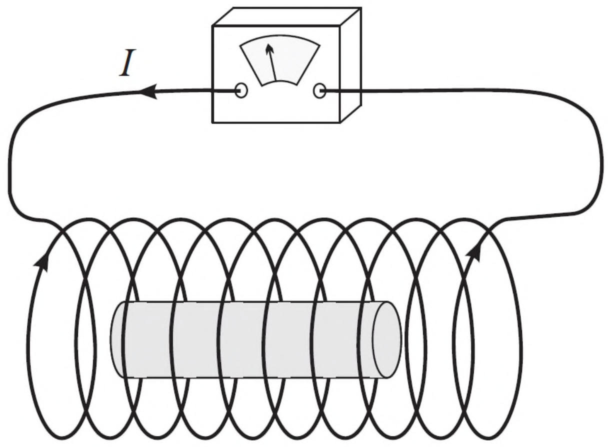
m = dipole moment = M V

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

neglect

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

Paramagnetism



Let's focus on isothermal and adiabatic processes:

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

Heat absorbed during isothermal change

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

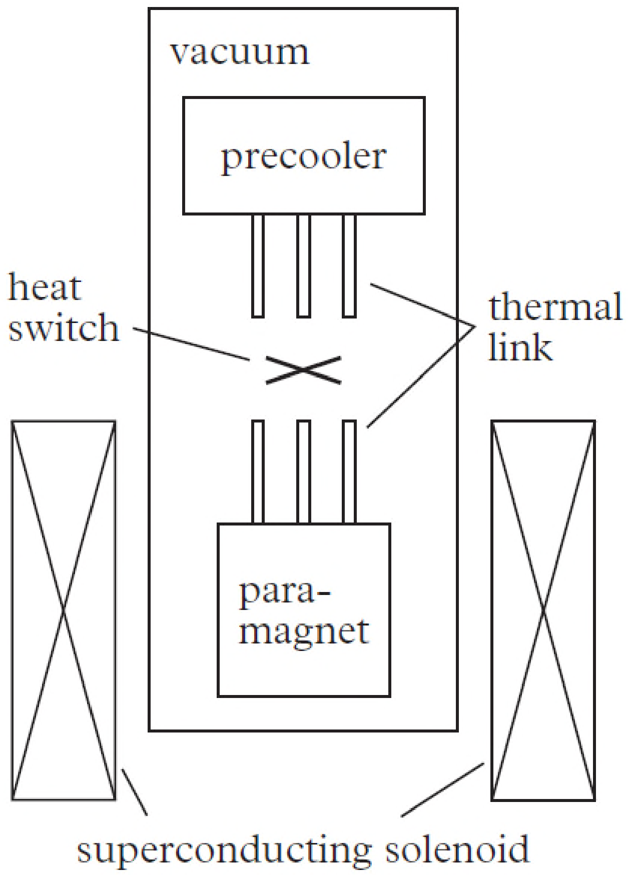
Temperature change during adiabatic process

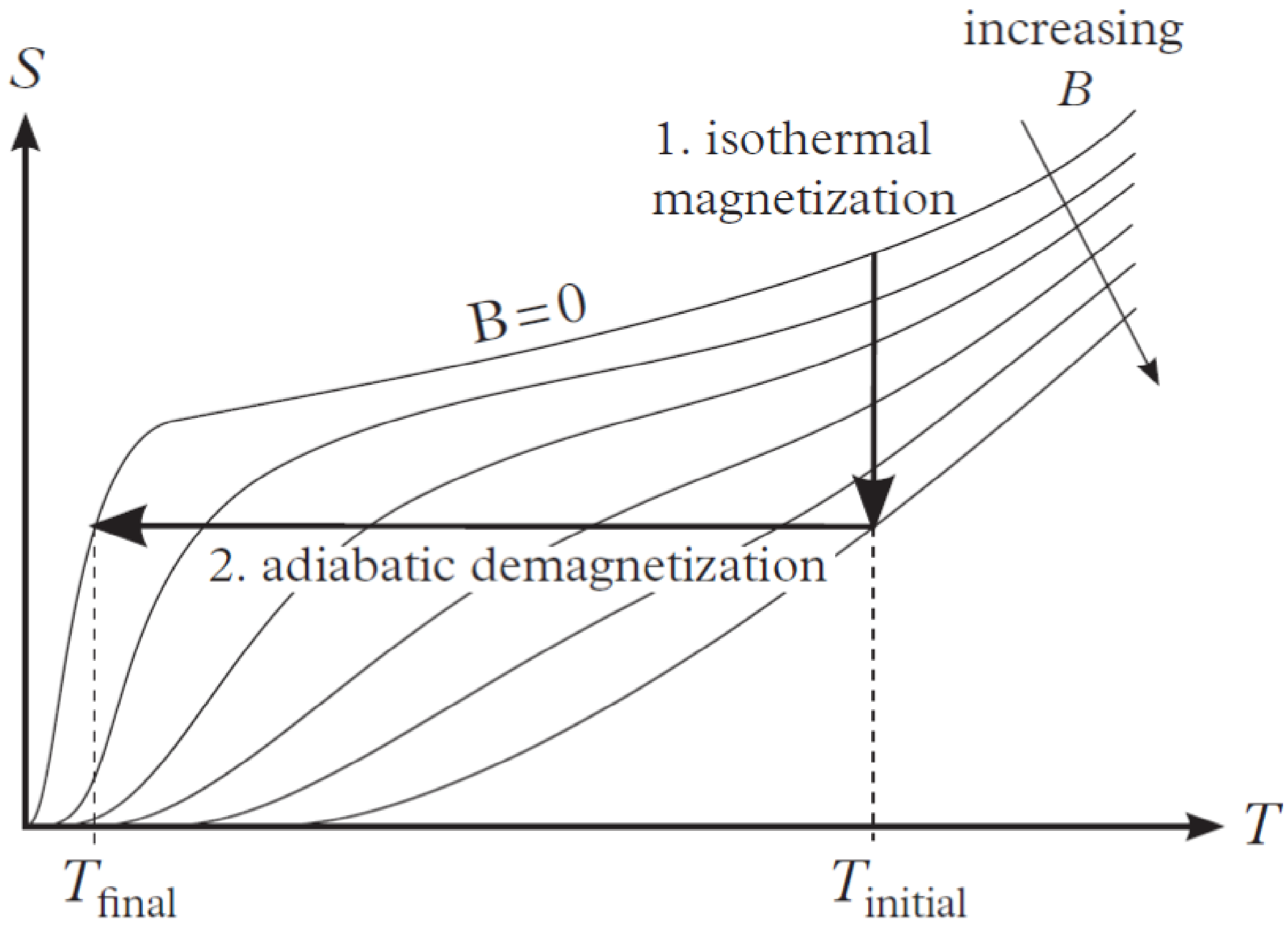
We will derive:

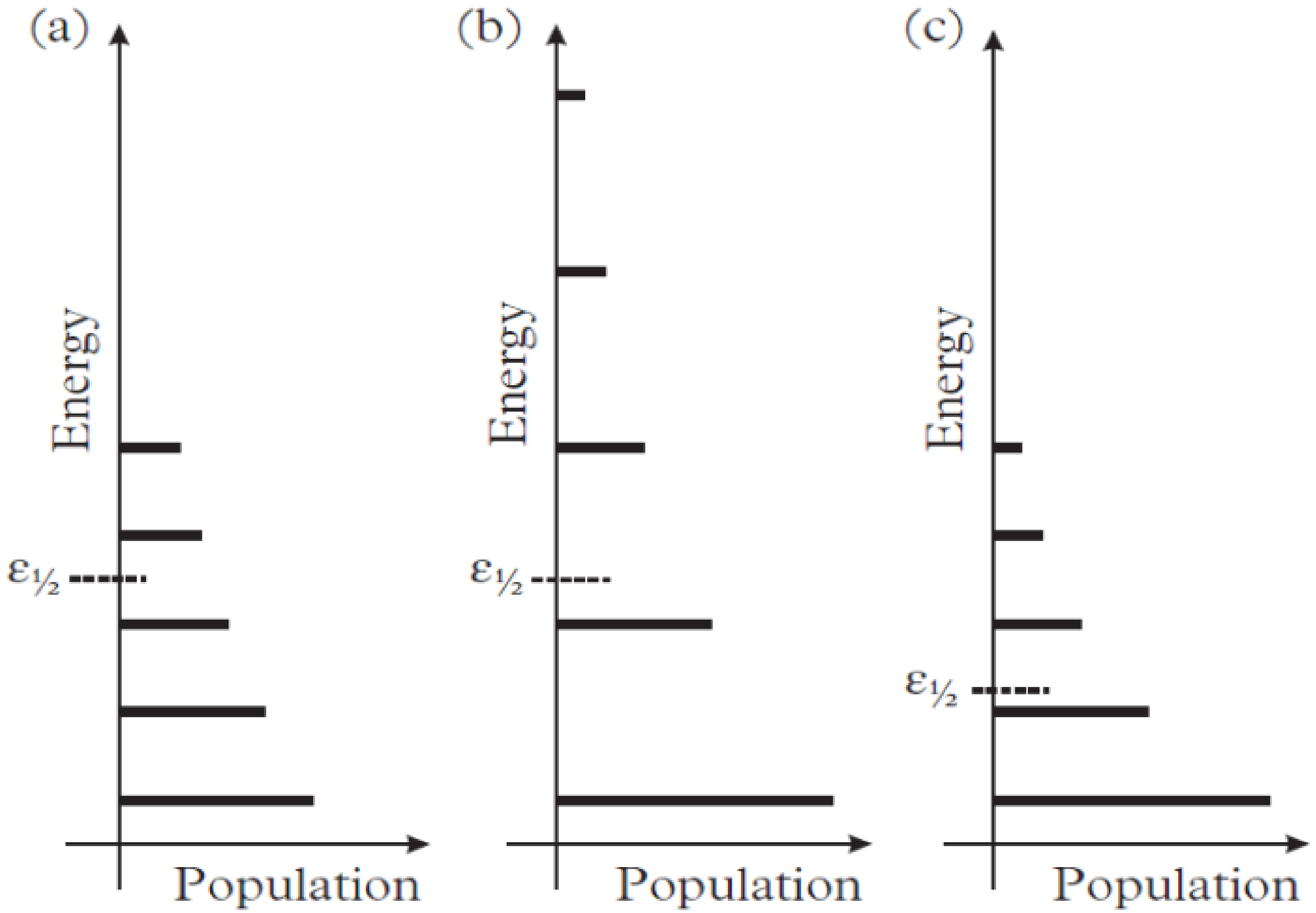
$$T \left.\frac{\partial S}{\partial B}\right|_T = \frac{TVB}{\mu_0} \left.\frac{\partial \chi}{\partial T}\right|_B$$

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

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.