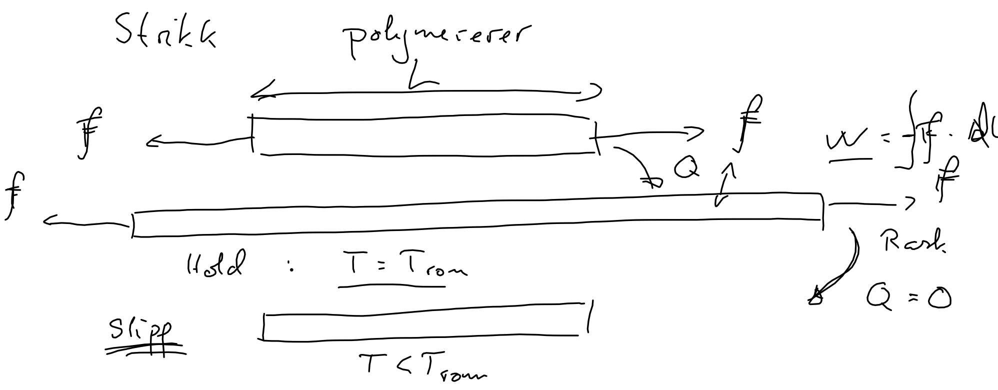
Strikk



$W = \int f \cdot dL$

$\Delta U = Q + W$

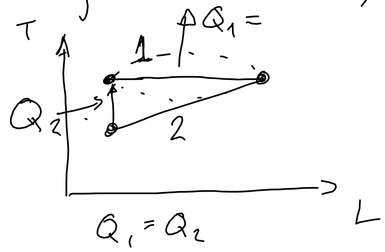
$0 = Q + \int f dL$

$\underline{Q = -W > 0}$

1\. lov $\Delta U = Q + W = 0$

=> Indre energi er ikke endret, men $\Delta T < 0$

$T\Delta S = Q$
Reversibel



$Q_1 = Q_2$

$$\boxed{1 \quad \frac{Q}{T} = \Delta S < 0}$$

2 rask prosess (irreversibel)

Liten endring i prosess 1 : strekking

$W = +f dL$ $\qquad W = -PdV$

Kvasistatisk / reversibel prosess:

1\. lov $dU = Q + W = Q - PdV$
TD1 $dU = TdS - PdV$
$\Big\} \Rightarrow Q = TdS$

For strikken TD1 $dU = TdS + fdL$.

$dU = \left(\frac{\partial U}{\partial S}\right)_L dS + \left(\frac{\partial U}{\partial L}\right)_S dL$

$$\left(\frac{\partial U}{\partial S}\right)_L = T \qquad \left(\frac{\partial U}{\partial L}\right)_S = f$$

Helmholtz

$F = U - TS$

$dF = dU - TdS - SdT$

$= \cancel{TdS} + fdL - \cancel{TdS} - SdT$

$= f dL - SdT$

$= \left(\frac{\partial F}{\partial L}\right)_T dL + \left(\frac{\partial F}{\partial T}\right)_L dT$

$$\boxed{\left(\frac{\partial F}{\partial L}\right)_T = f} \qquad \left(\frac{\partial F}{\partial T}\right)_L = -S$$

$\cdot\ dU = TdS + fdL$

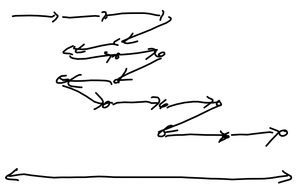
$\cdot\ dS = \frac{1}{T}dU - \frac{f}{T}dL$

$= \left(\frac{\partial S}{\partial U}\right)_L dU + \left(\frac{\partial S}{\partial L}\right)_U dL$

$$\boxed{\left(\frac{\partial S}{\partial L}\right)_U = -\frac{f}{T} < 0} \qquad \left(\frac{\partial S}{\partial U}\right)_L = \frac{1}{T}$$

$$\frac{\partial S}{\partial L} < 0 \qquad \boxed{f = -T\left(\frac{\partial S}{\partial L}\right)_U}$$

monomerer



L

l lengden av monomer

$L = N_R \cdot l + N_L \cdot l$

↑ makro

Hvert element har mikro tilstand $s_i = \begin{cases} +1 & \text{høyre} \\ -1 & \text{venstre} \end{cases}$

$$L = l \sum_i s_i = l(N_R - N_L)$$

$$N_R = N - N_L \Rightarrow L = l(N - N_L - N_L) = l(N - 2N_L)$$

$$N_L = \left(\frac{L}{l} - N\right)/2 \qquad \underline{N_R = \left(\frac{L}{l} + N\right)/2}$$

Hvor mange måter kan vi ordne polymeren for en gitt N_R, N

= Antall måter vi kan velge N_R tilstander fra N

$$\Omega(N_R, N) = \binom{N}{N_R} = \frac{N!}{N_R!(N - N_R)!}$$

Stirling $\ln(N!) = N \ln N - N$

$$\ln \Omega = N \ln N - \cancel{N} - \left[N_R \ln N_R - \cancel{N_R} + (N - N_R)\ln(N - N_R) - \cancel{(N - N_R)}\right]$$

$$= N \ln N - N_R \ln N_R - (N - N_R)\ln(N - N_R)$$

Entropien til et isolert system med $\underline{N, V, U \text{ konstant}}$

$$S = k \ln \Omega$$

$$S = k\left(N \ln N - N_R \ln N_R - (N - N_R)\ln(N - N_R)\right) \qquad f = -T\left(\frac{\partial S}{\partial L}\right)_U$$

$$N_R = \left(\frac{L}{l} + N\right)/2 \qquad f = -T\left(\frac{\partial S}{\partial N_R}\right)_U \frac{\partial N_R}{\partial L} \qquad \frac{\partial N_R}{\partial L} = \frac{1}{2l}$$

$$\left(\frac{\partial S}{\partial N_R}\right)_U = k\left(-\ln N_R - 1 + \ln(N - N_R) + \frac{(N - N_R)}{N - N_R}\right)$$

$$= k\left(\ln(N - N_R) - \ln N_R\right) = k \ln \frac{N - N_R}{N_R}$$

$$\boxed{f = \frac{kT}{2l} \ln \frac{N_R}{N - N_R} = \frac{kT}{2l} \ln \frac{Nl + L}{Nl - L}}$$

$$f = \left(\frac{\partial F}{\partial L}\right)_T \qquad F = -kT \ln Z \qquad \text{kanonisk}$$

$$Z(T, L, N) = \sum_i e^{-\varepsilon_i / kT}$$

Hver monomer har energien $\Delta\varepsilon$ uavhengig av s_i $\Rightarrow$ $\varepsilon_i = N\Delta\varepsilon$

Implikasjon (ε_i) U til polymer er ikke avh. av lengden

$$Z = \sum_i e^{-\Delta\varepsilon \cdot N / kT} = \Omega(N_R, N) \cdot e^{-N\Delta\varepsilon / kT}$$

$$f = \left(\frac{\partial F}{\partial L}\right)_T = kT \frac{\partial \ln Z}{\partial L} = -T \left(\frac{\partial S}{\partial L}\right)_{U,N}$$