

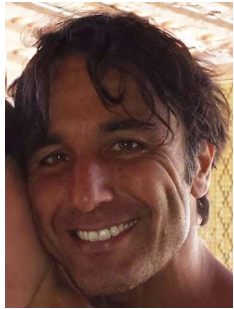
Temperature effects in the cohesion-decohesion process: applications to biophysics and material science

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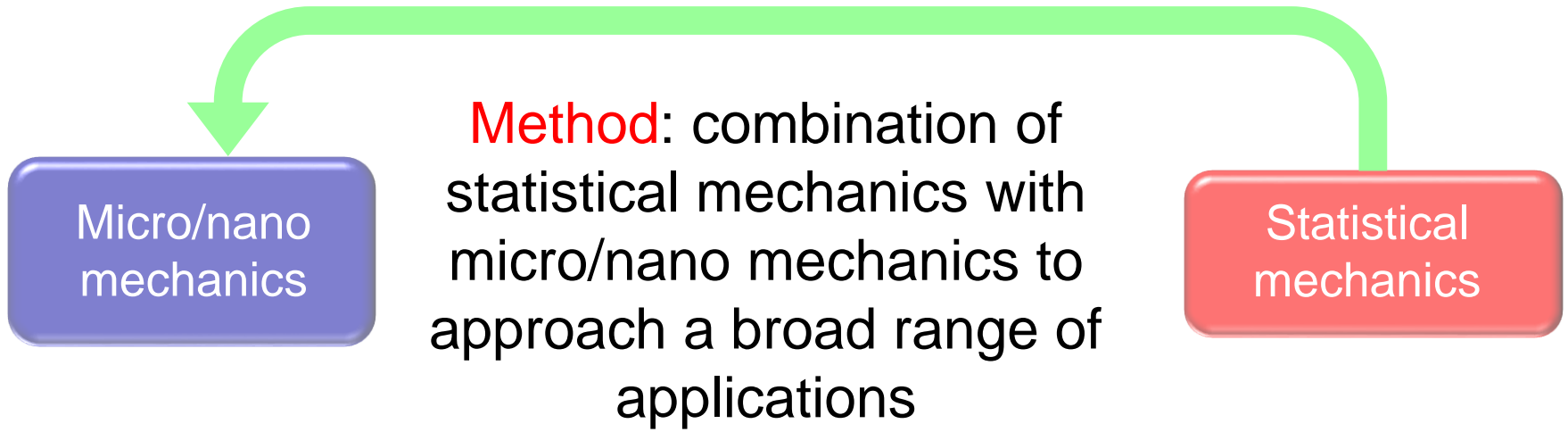
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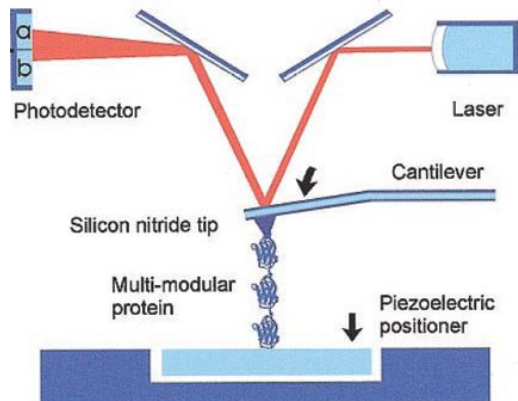
Pier Luca Palla
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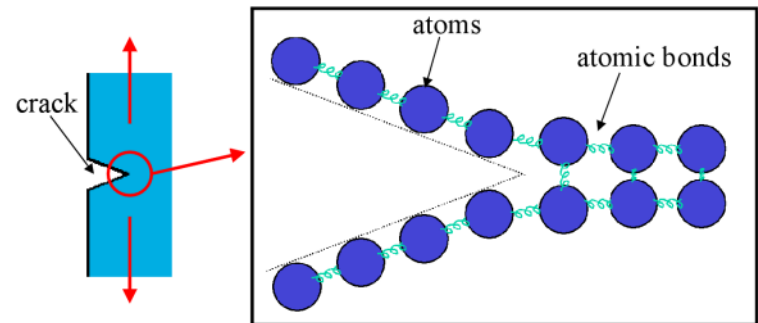
Context: study of mechanical microinstabilities (conformational transitions or ruptures) in small systems with important effects of the temperature



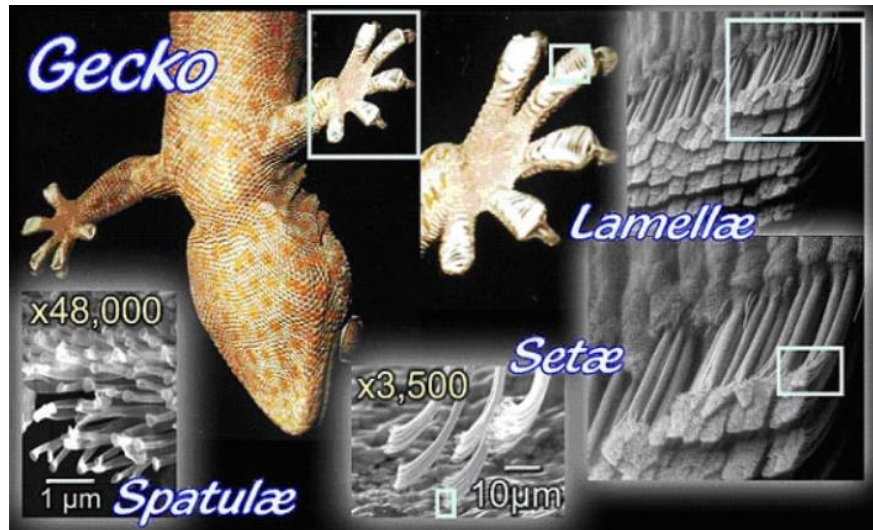
Biophysics



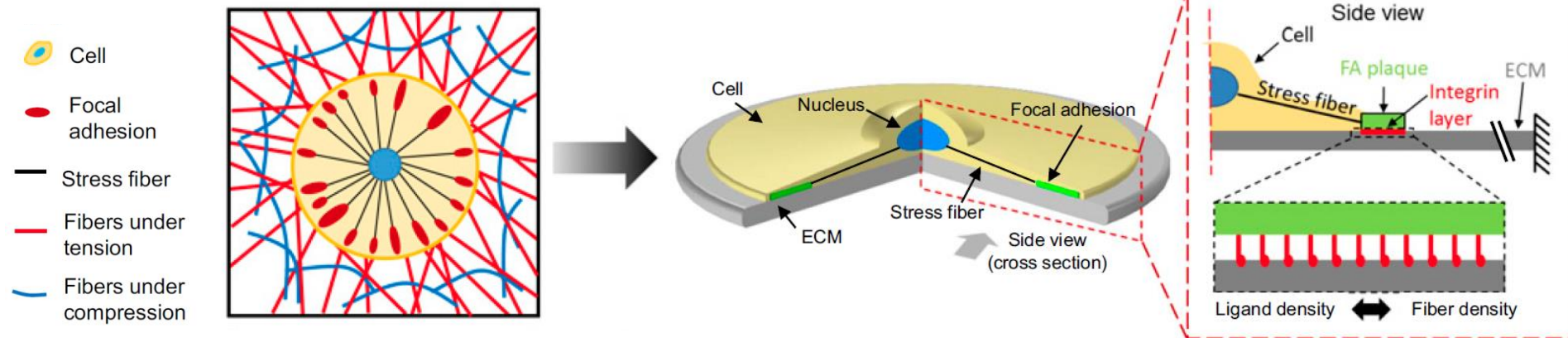
Material science



Adhesion in biology

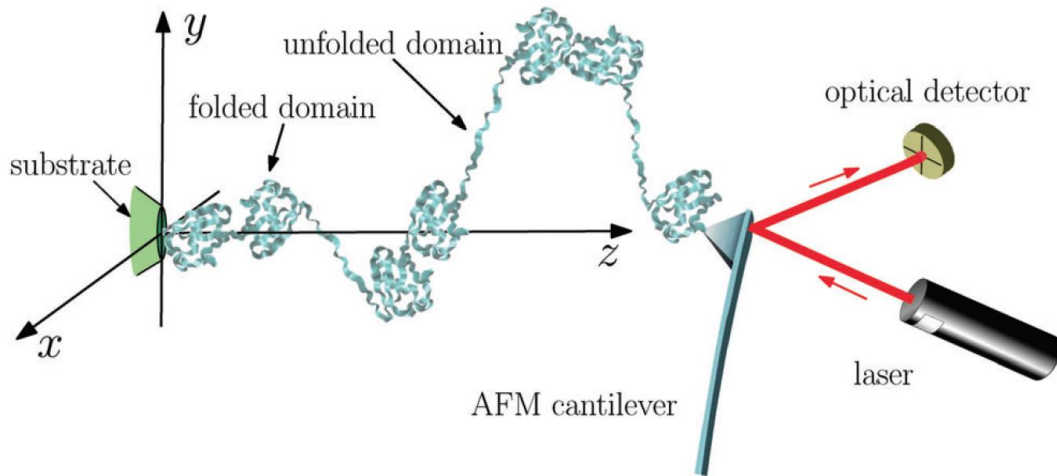


K. Autumn, N. Gravish,
Gecko adhesion: evolutionary nanotechnology,
Philosophical Transaction of the
Royal Society, 2008.

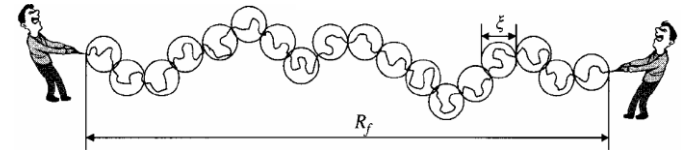


Xuan Cao et al. Proc Natl Acad Sci U S A. **114** (23): E4549-E4555 (2017)

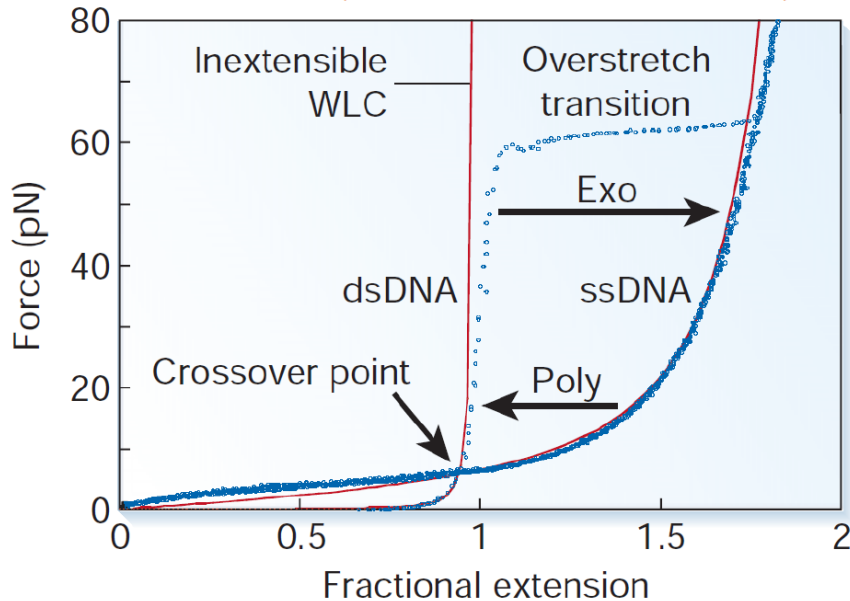
Nanomechanics of macromolecules



Single molecule force spectroscopy

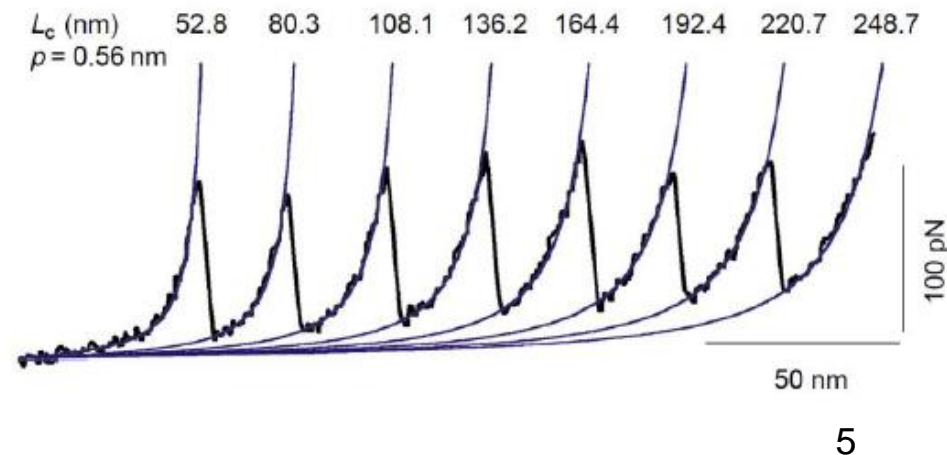


DNA (*Nature* 421, 423, 2003)

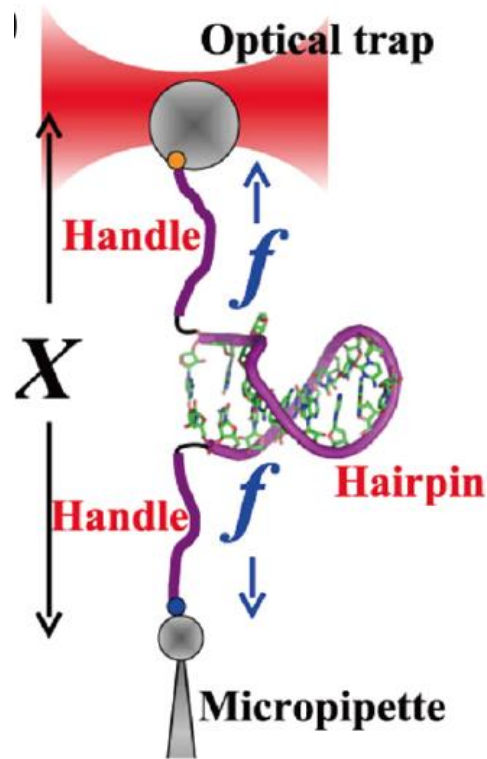


TIBS 24, p. 379–384, 1999

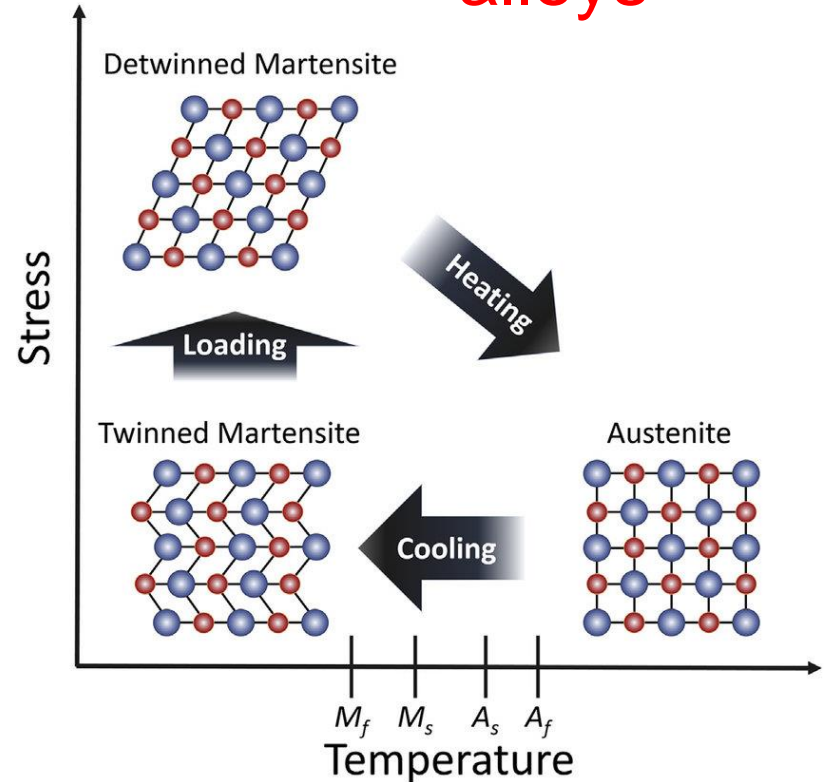
Human tenascin-C, N=7



Hairpins unzipping



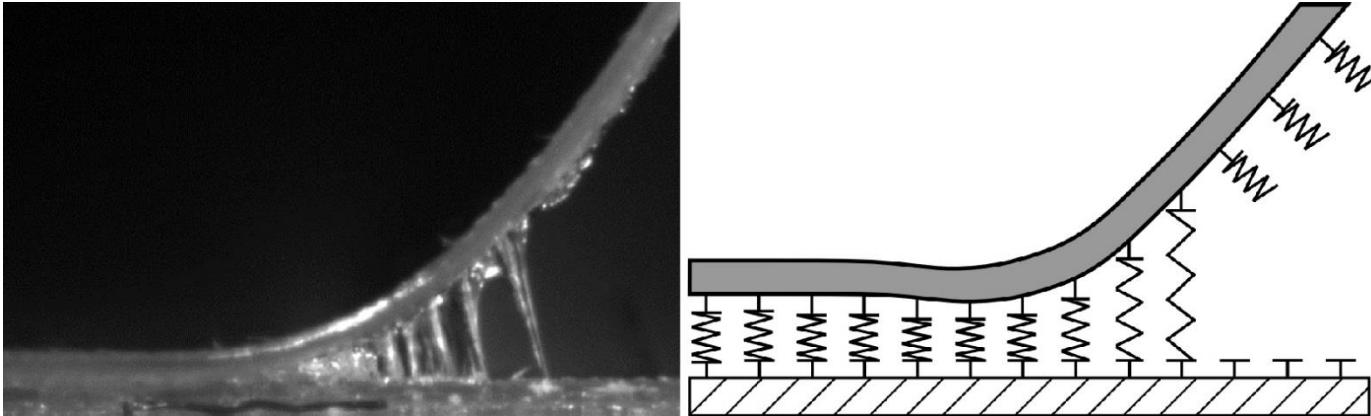
Phase transformations in shape memory alloys



Physics Reports 631 (2016) 1-41

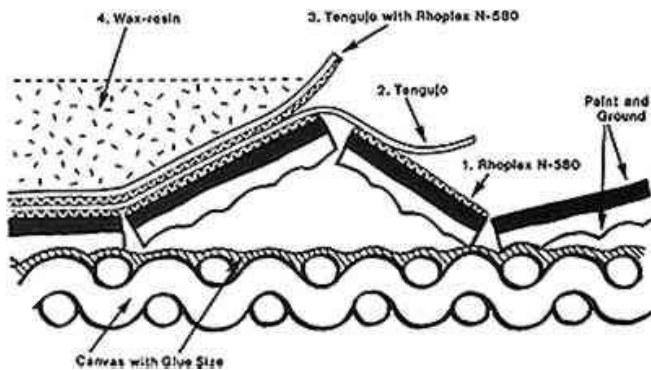
Composites Part B 86 (2016) 285-298

Adhesion/deadhesion in micro-nano technology...



R Villey, et al., *Soft Matter*, 11, 3480-91 (2015)

...treatment of old paintings



JAIC 1992, Volume 31, Number 2,
Article 2 (pp. 161 to 173)

...glaciology



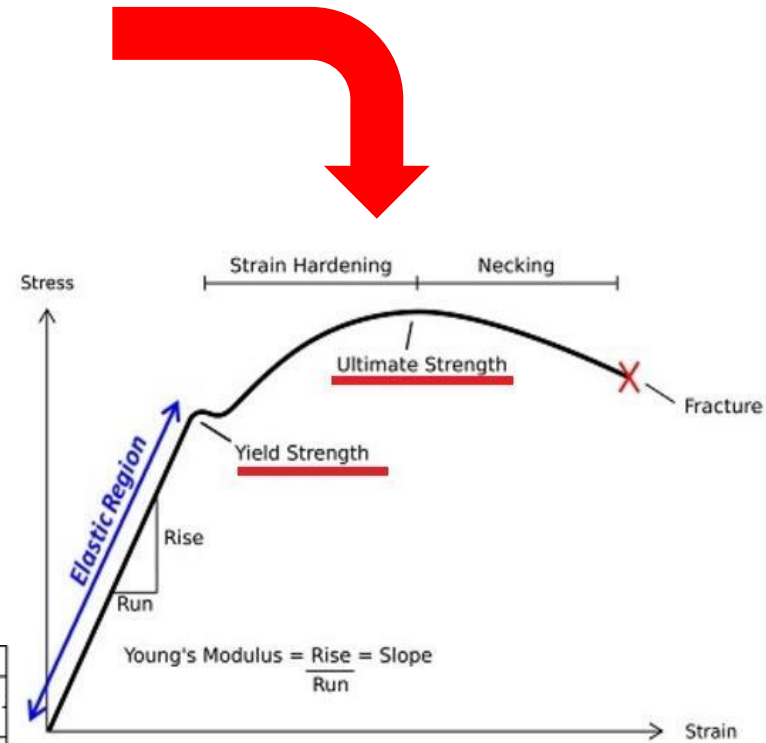
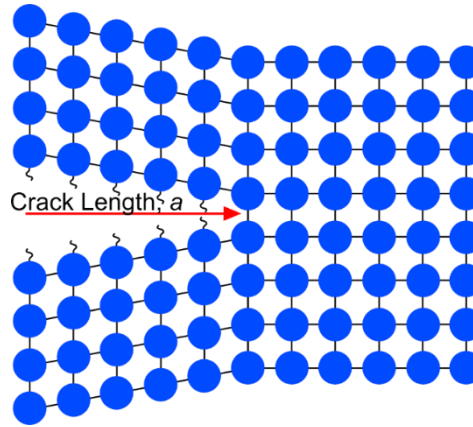
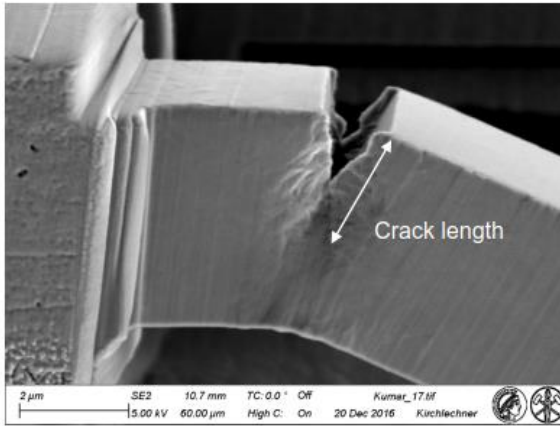
Crevasse, Emmons Glacier,
Washington

...geology

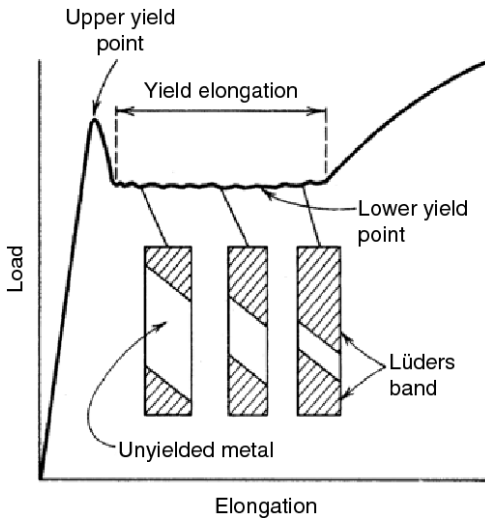


Crevice, Wyoming

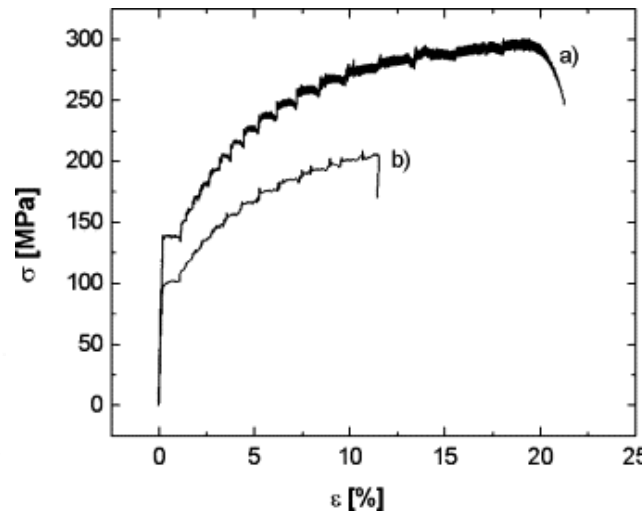
Fracture mechanics



Plastic phenomena



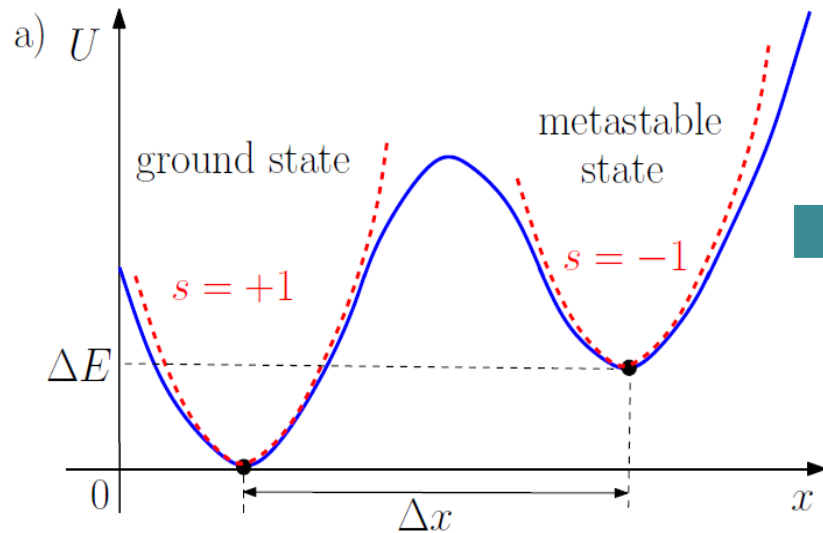
Luder band



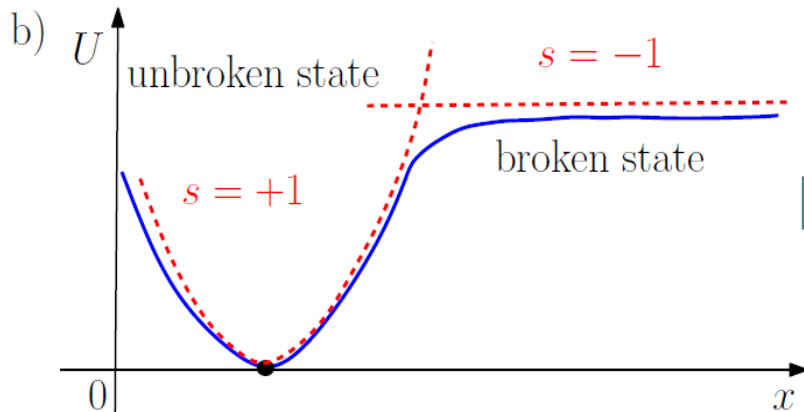
Portevin Le Chatelier effect

Stress - strain curve for a ductile material

Taxonomy of microinstabilities

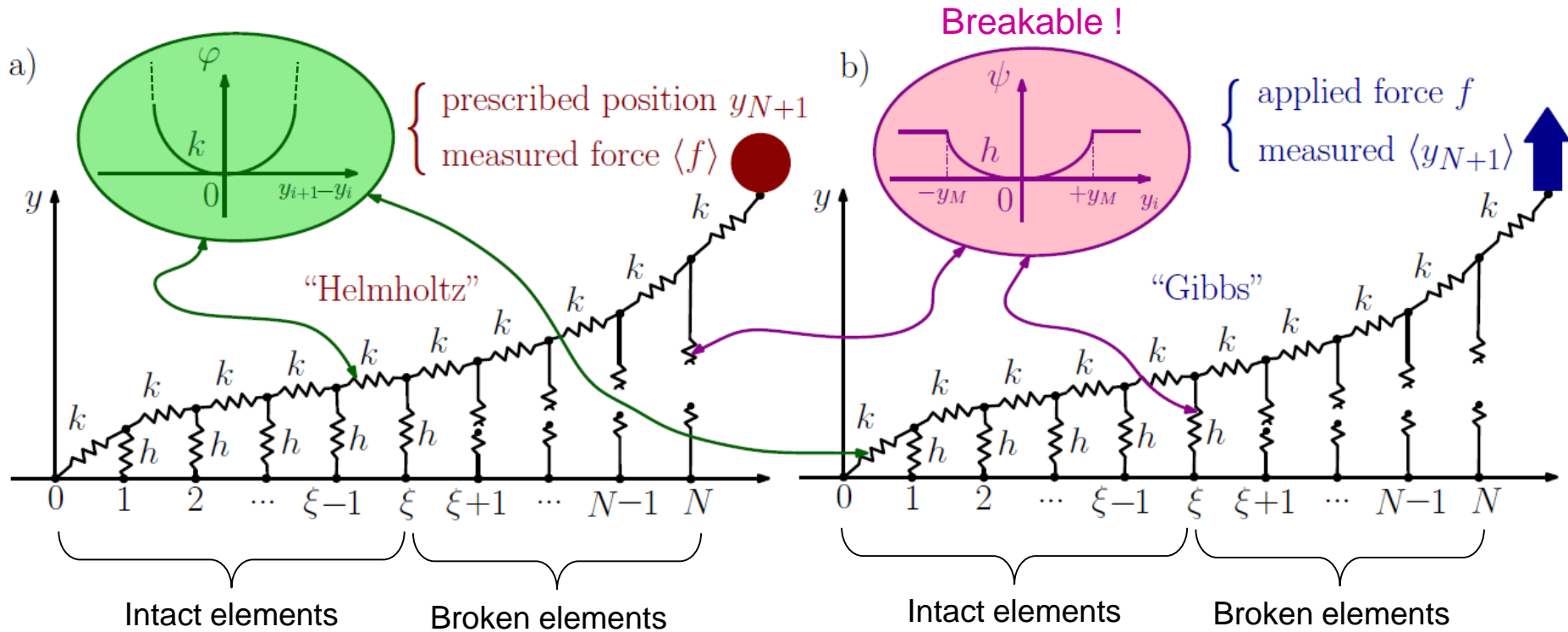


Bistable (or multistable) behavior between one **ground state** and one (or more) **metastable state**.
Examples: conformational transitions in polymers or martensitic transformations in solids.



Transitions between the **broken or unbroken states** of some breakable units of the system.
Examples: unzipping of hairpins, denaturation of macromolecules and peeling of films.

Model of cohesion-decohesion



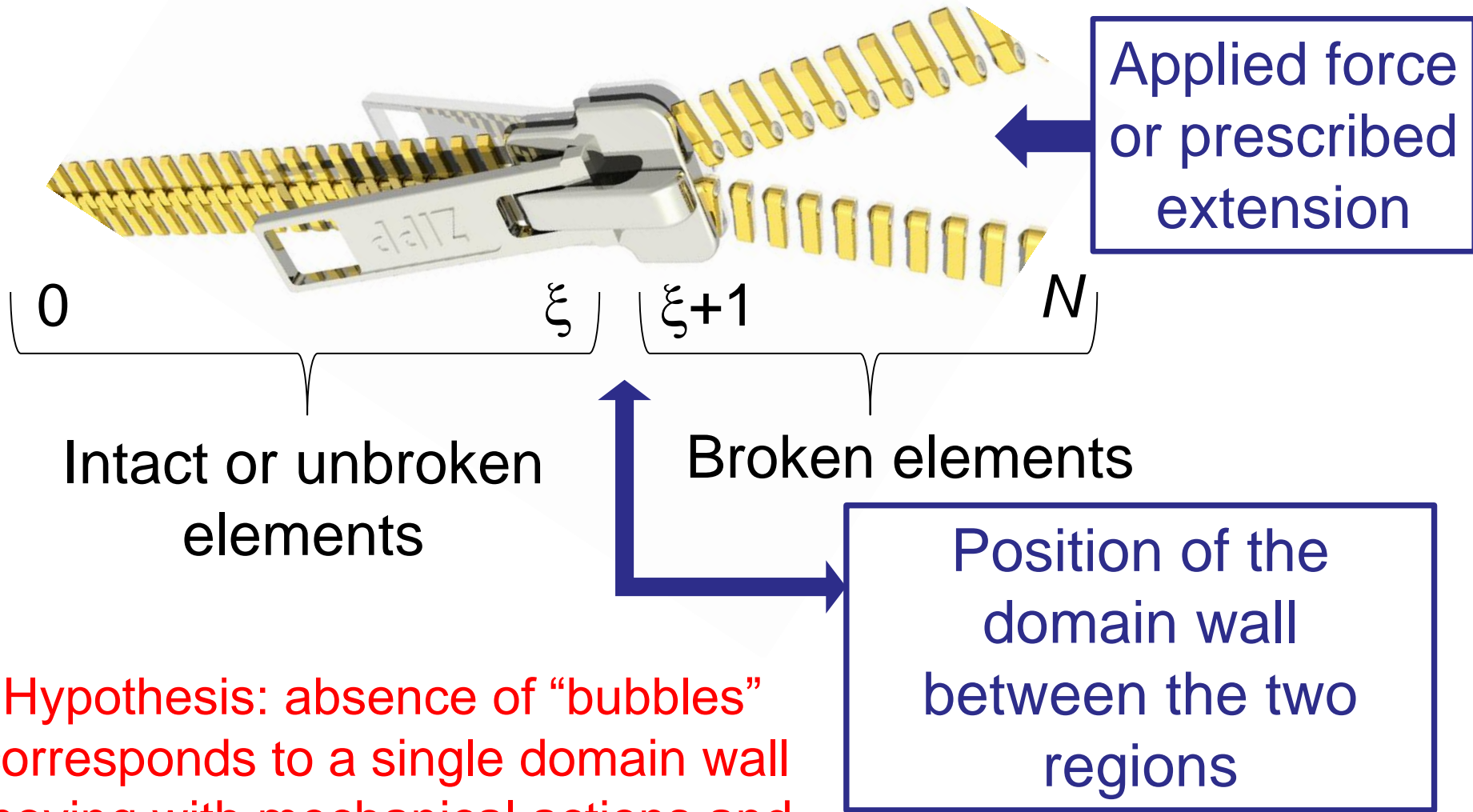
**Helmholtz ensemble
(prescribed position)**

**Gibbs ensemble
(applied force)**

Equilibrium statistical mechanics (rate-independent process)

Application to : **Hairpins unzipping** and
Strength of materials

Hypothesis: zipper model



Hypothesis: absence of “bubbles” corresponds to a single domain wall moving with mechanical actions and temperature

$\eta = h/k$ Ratio between elastic constants

ξ Number of intact elements

\vec{y} Vertical positions of the elements

$$\Phi(\vec{y}, \xi; y_{N+1}) = \frac{1}{2} k \vec{y}^T \mathcal{A}_N^\xi(\eta) \vec{y} - k y_{N+1} \vec{v}^T \vec{y} + \frac{1}{2} k y_{N+1}^2 + \frac{1}{2} k \eta (N - \xi) y_M^2,$$

Potential energy of the system

Where $\vec{v} = (0, 0, 0, \dots, 0, 1) \in \mathbb{R}^N$ and $\mathcal{A}_N^\xi(\eta)$ is a tridiagonal matrix

$$\mathcal{A}_N^\xi(\eta) = \begin{bmatrix} a_1 & -1 & 0 & \dots & 0 \\ -1 & a_2 & -1 & \ddots & \vdots \\ 0 & -1 & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & a_{N-1} & -1 \\ 0 & \dots & 0 & -1 & a_N \end{bmatrix} \in \mathcal{M}_{N,N}(\mathbb{R})$$

$$\text{with } \begin{cases} a_1 = \dots = a_\xi = 2 + \eta, \\ a_{1+\xi} = \dots = a_N = 2. \end{cases}$$

Properties of $\mathcal{A}_N^\xi(\eta)$

$$\det \mathcal{A}_N^\xi(\eta) = (N - \xi + 1)G(\xi + 1) - (N - \xi)G(\xi)$$

$$1 - \vec{v}^T \left[\mathcal{A}_N^\xi(\eta) \right]^{-1} \vec{v} = \frac{G(\xi + 1) - G(\xi)}{(N - \xi + 1)G(\xi + 1) - (N - \xi)G(\xi)}$$

where

$$G(z) = \frac{1}{\sqrt{\Delta}} \left(\frac{2 + \eta + \sqrt{\Delta}}{2} \right)^z - \frac{1}{\sqrt{\Delta}} \left(\frac{2 + \eta - \sqrt{\Delta}}{2} \right)^z$$

$$\text{with } \Delta = \eta^2 + 4\eta$$

Helmholtz ensemble (prescribed position)

Partition function

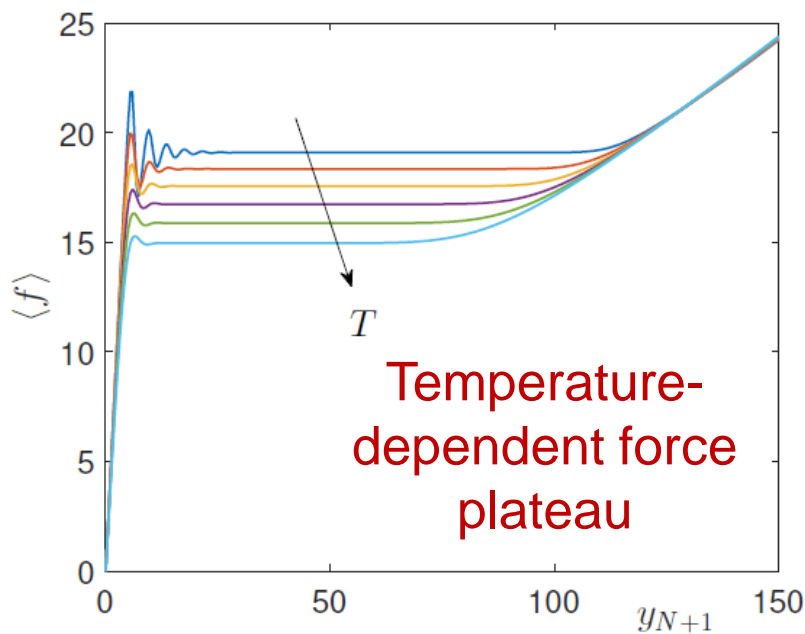
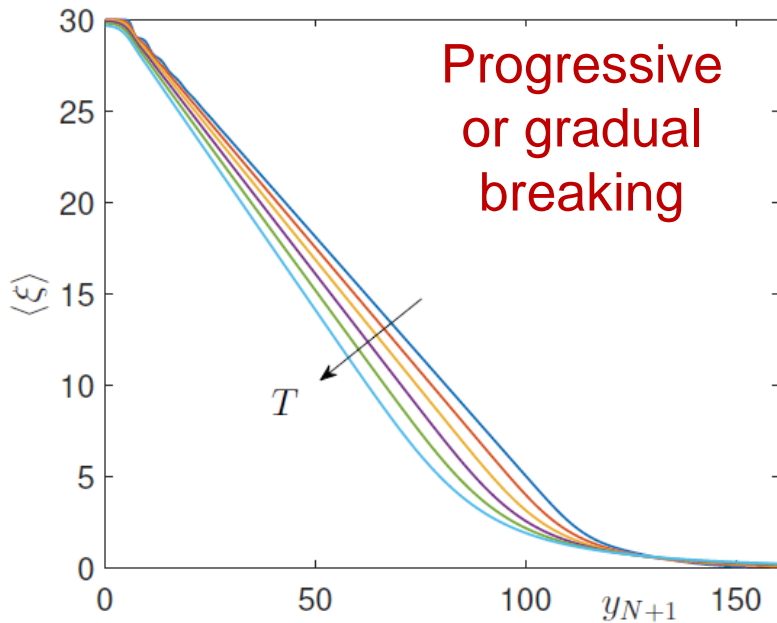
$$Z_H(y_{N+1}) = \int_{\mathbb{R}^N} \sum_{\xi=0}^N e^{-\frac{\Phi(\vec{y}, \xi; y_{N+1})}{K_B T}} d\vec{y}$$

Average number of intact
(or unbroken) elements

$$\langle \xi \rangle = \frac{1}{Z_H} \sum_{\xi=0}^N \xi \sqrt{\frac{(2\pi K_B T)^N}{k^N \det \mathcal{A}_N^\xi(\eta)}} e^{-\frac{ky_M^2}{2K_B T} \eta(N-\xi)} \times e^{-\frac{ky_{N+1}^2}{2K_B T} \left\{ 1 - \vec{v}^T [\mathcal{A}_N^\xi(\eta)]^{-1} \vec{v} \right\}}$$

Average value of the force

$$\langle f \rangle = ky_{N+1} \frac{1}{Z_H} \sum_{\xi=0}^N \sqrt{\frac{(2\pi K_B T)^N}{k^N \det \mathcal{A}_N^\xi(\eta)}} e^{-\frac{ky_M^2}{2K_B T} \eta(N-\xi)} \times \left\{ 1 - \vec{v}^T [\mathcal{A}_N^\xi(\eta)]^{-1} \vec{v} \right\} e^{-\frac{ky_{N+1}^2}{2K_B T} \left\{ 1 - \vec{v}^T [\mathcal{A}_N^\xi(\eta)]^{-1} \vec{v} \right\}}$$



Gibbs ensemble (applied force)

Partition function

$$Z_G(f) = \int_{\mathbb{R}^{N+1}} \sum_{\xi=0}^N e^{-\frac{\Phi(y, \xi; y_{N+1})}{K_B T}} e^{\frac{f y_{N+1}}{K_B T}} dy dy_{N+1}$$

$$= \int_{-\infty}^{+\infty} Z_H(y_{N+1}) e^{\frac{f y_{N+1}}{K_B T}} dy_{N+1},$$

Average number of intact (or unbroken) elements

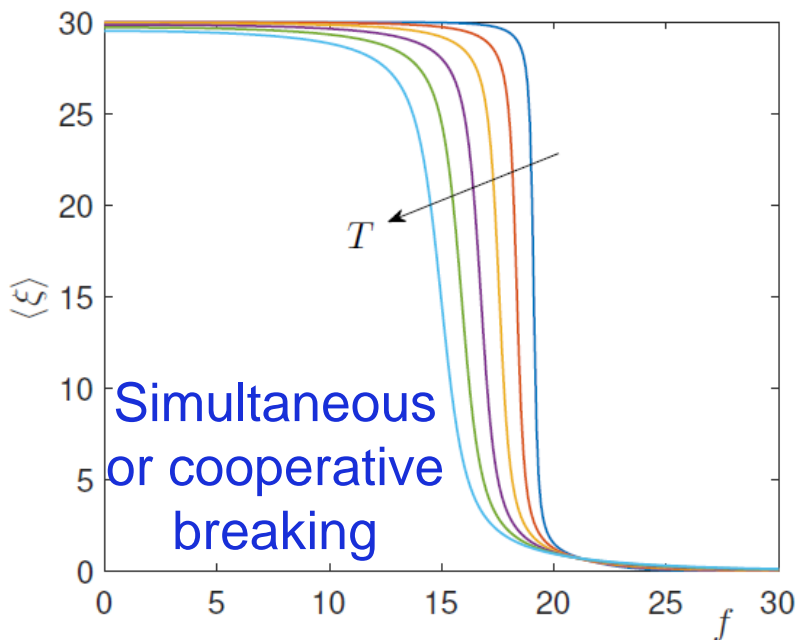
$$\langle \xi \rangle = \frac{1}{Z_G} \sum_{\xi=0}^N \xi \sqrt{\frac{(2\pi K_B T/k)^{N+1}}{\det \mathcal{A}_N^\xi(\eta) \left\{ 1 - \bar{v}^T [\mathcal{A}_N^\xi(\eta)]^{-1} \bar{v} \right\}}}$$

$$\times e^{-\frac{k y_M^2}{2K_B T} \eta(N-\xi)} e^{\frac{f^2}{2kK_B T} \left\{ 1 - \bar{v}^T [\mathcal{A}_N^\xi(\eta)]^{-1} \bar{v} \right\}^{-1}}.$$

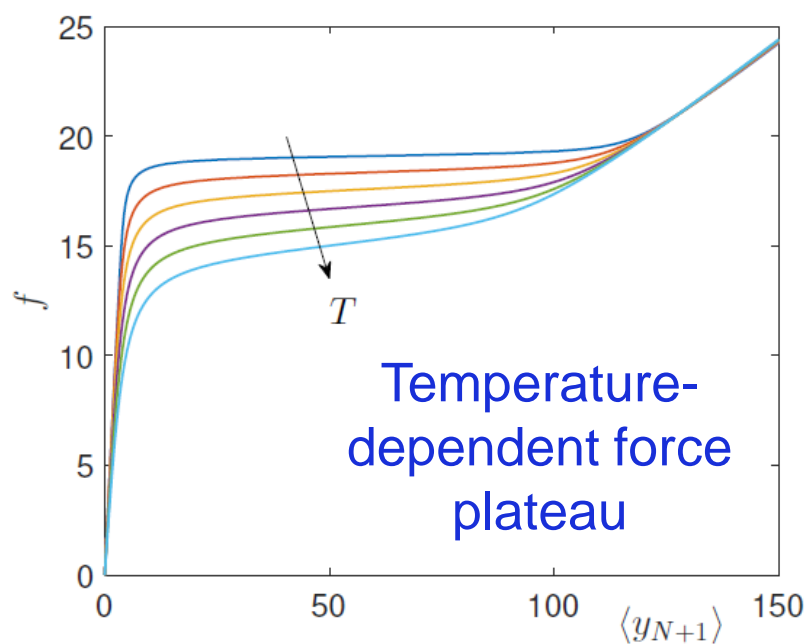
Average value of the extension

$$\langle y_{N+1} \rangle = \frac{f}{k} \frac{1}{Z_G} \sum_{\xi=0}^N \sqrt{\frac{(2\pi K_B T/k)^{N+1}}{\det \mathcal{A}_N^\xi(\eta) \left\{ 1 - \bar{v}^T [\mathcal{A}_N^\xi(\eta)]^{-1} \bar{v} \right\}^3}}$$

$$\times e^{-\frac{k y_M^2}{2K_B T} \eta(N-\xi)} e^{\frac{f^2}{2kK_B T} \left\{ 1 - \bar{v}^T [\mathcal{A}_N^\xi(\eta)]^{-1} \bar{v} \right\}^{-1}}.$$



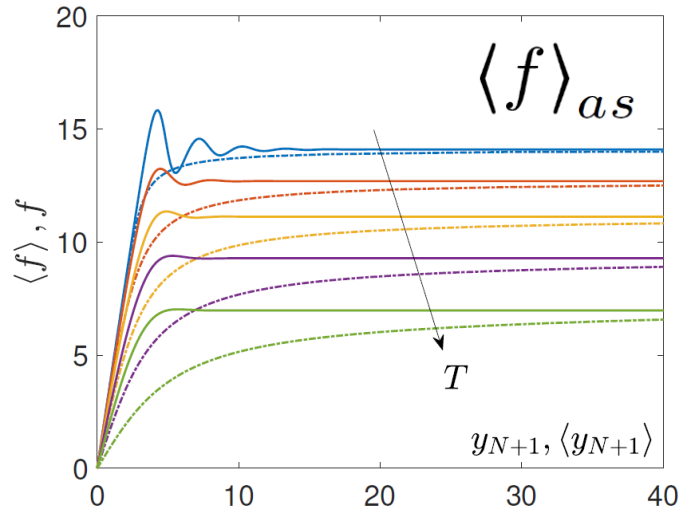
Simultaneous
or cooperative
breaking



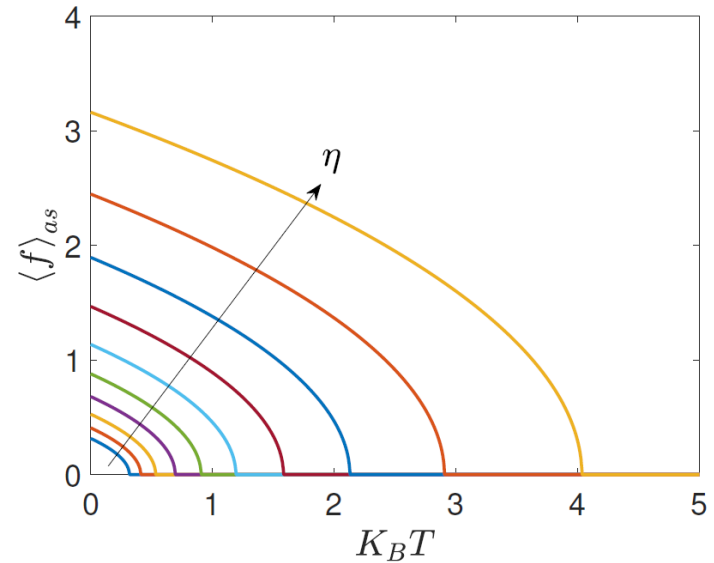
Temperature-
dependent force
plateau

Thermodynamic limit ($N \rightarrow \infty$)

$$\sum_{\xi=0}^N \phi(\xi) \longrightarrow \int_0^N \phi(\xi) d\xi \quad (\text{asymptotic methods})$$



Solid lines: Helmholtz
Dashed lines: Gibbs



Phase transition

$$\langle f \rangle_{as} = \sqrt{k h y_M} \sqrt{1 - \frac{T}{T_c}}$$

Critical force

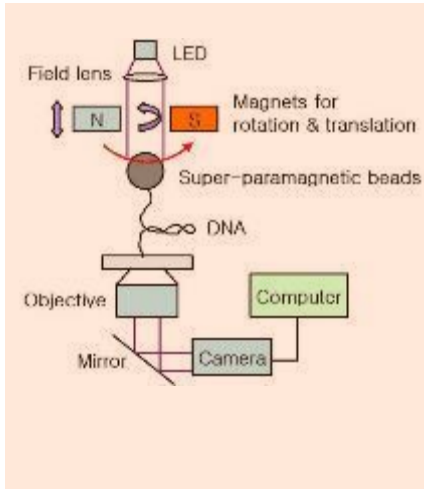
with

$$T_c = \frac{1}{\frac{K_B}{h y_M^2} \log \frac{2 + \eta + \sqrt{\eta^2 + 4\eta}}{2}}$$

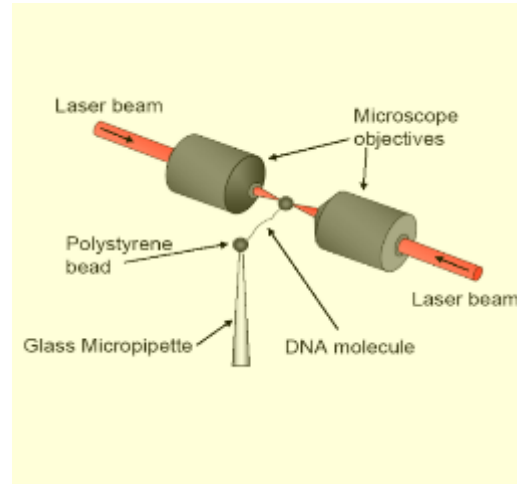
Critical or denaturation temperature

Force-spectroscopy methods (Neuman and Nagy, 2008)

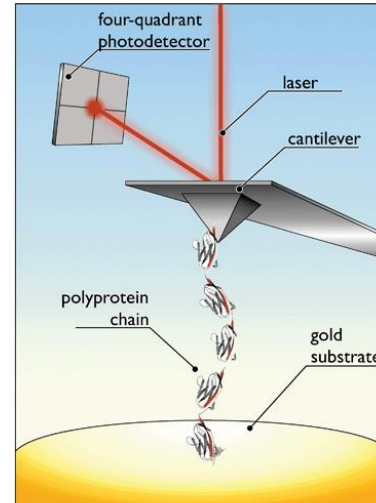
Magnetic tweezers



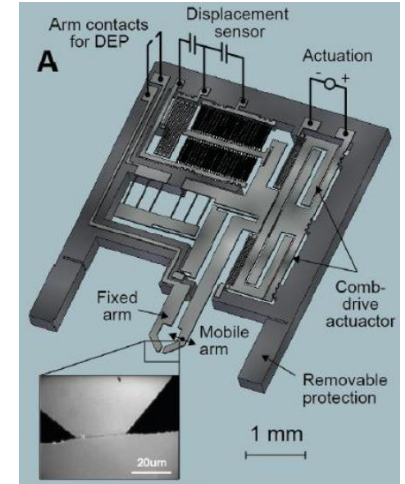
Optical tweezers



Atomic force microscope

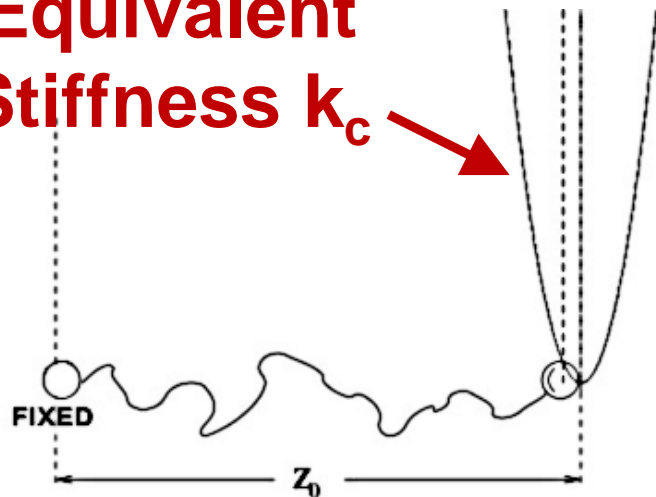


MEMS



Devices with variable stiffness k_c ($10^{-5} - 10^4$ pN·nm $^{-1}$)

Equivalent Stiffness k_c

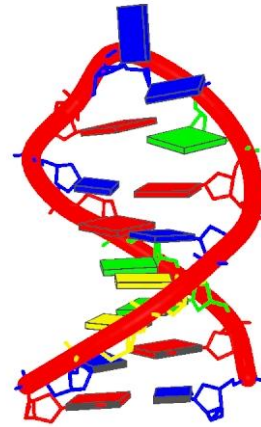
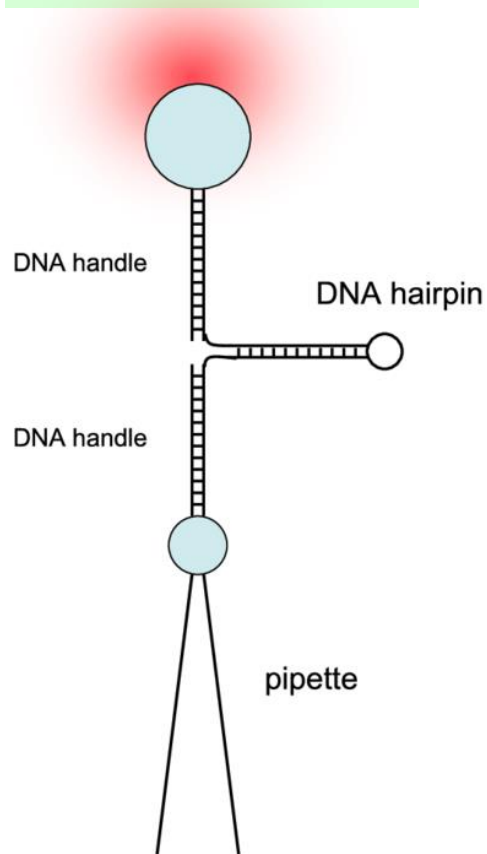


Soft cantilever → Gibbs ensemble

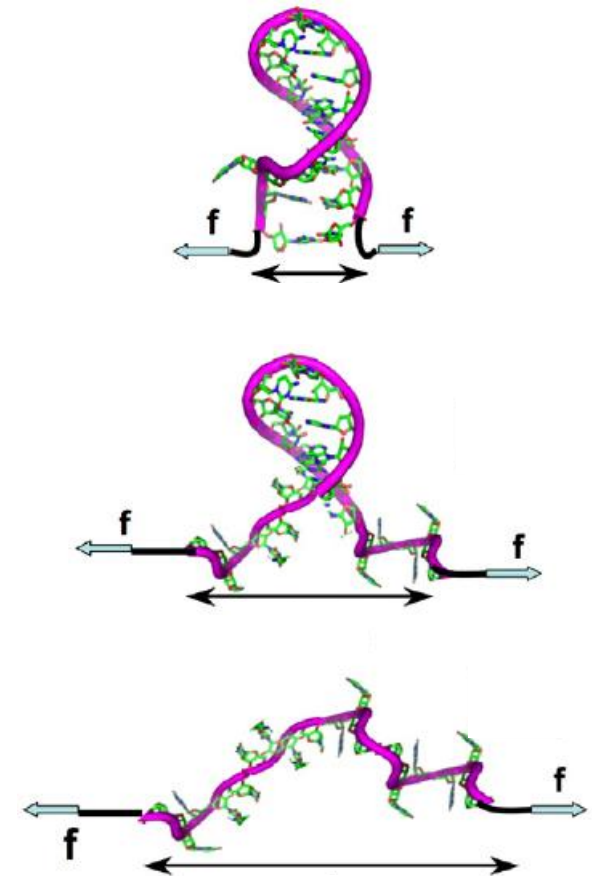
Hard cantilever → Helmholtz ensemble

Hairpins

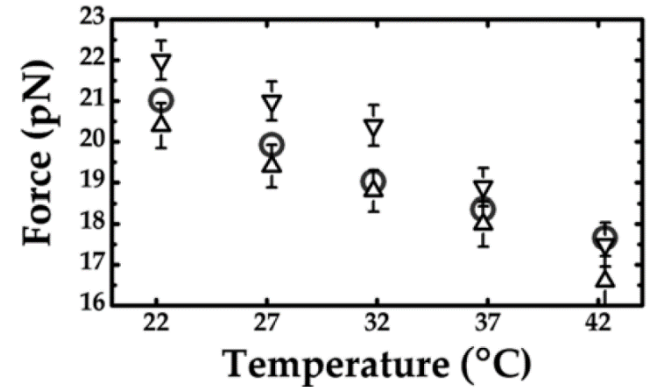
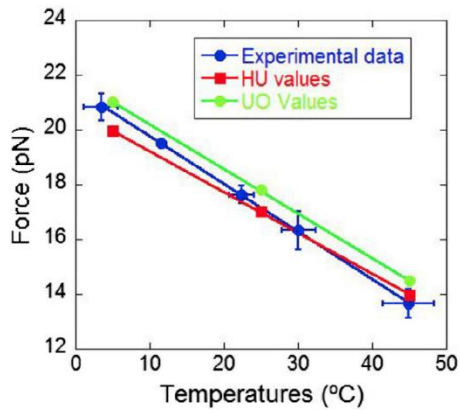
Optical tweezers



Detachment experiment

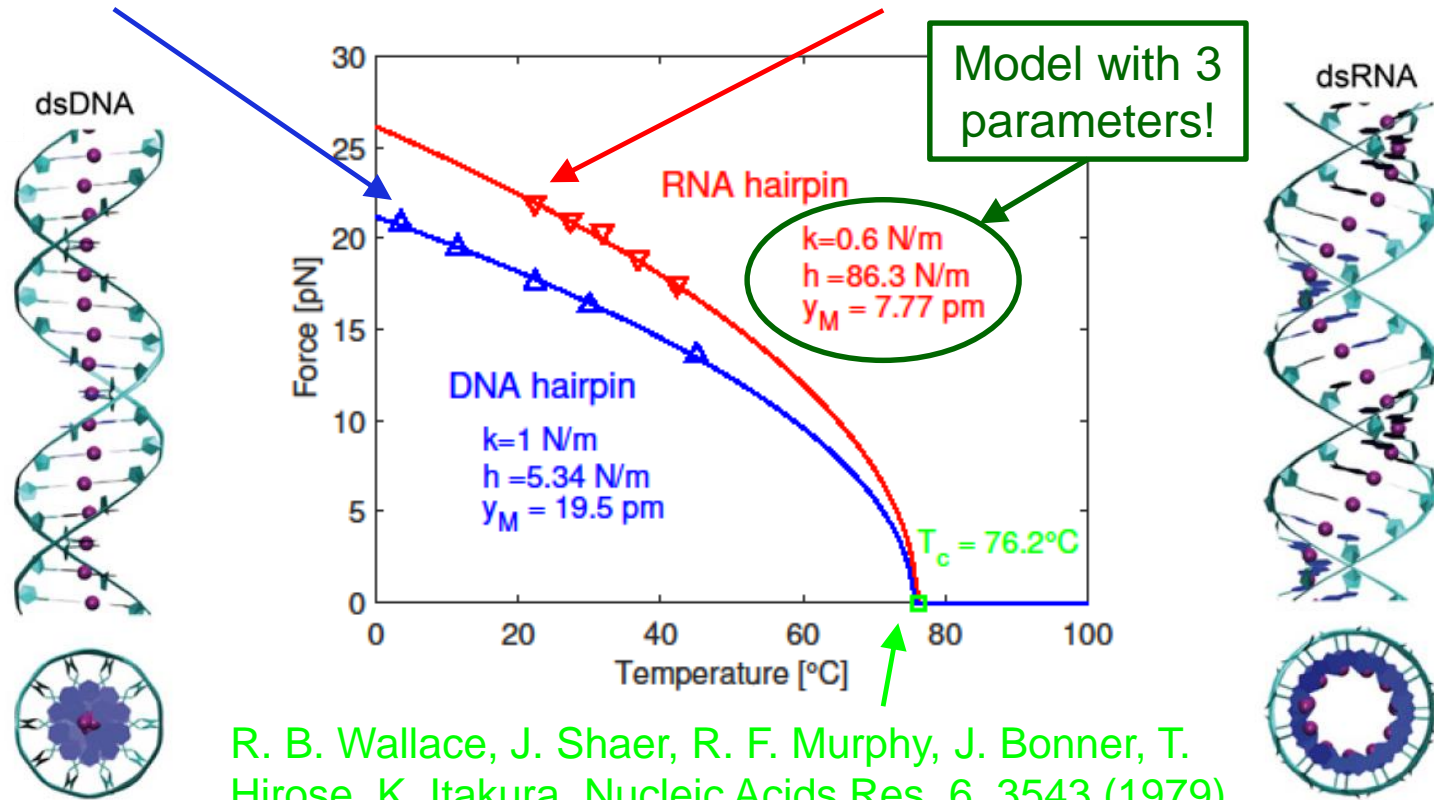


Hairpins



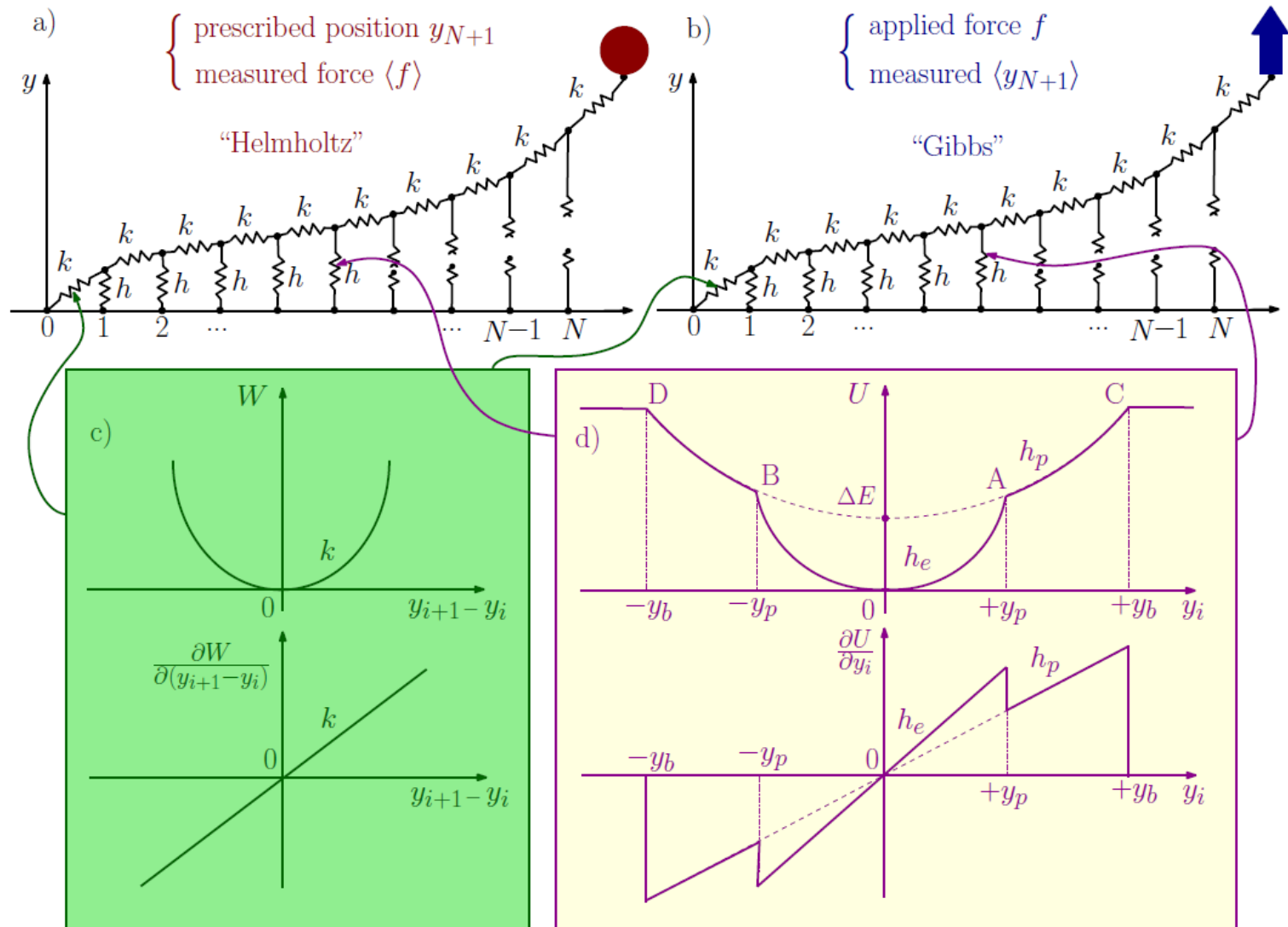
S. de Lorenzo, M. Ribezzi-Crivellari, J. R. Arias-Gonzalez, S. B. Smith, and F. Ritort, *Biophysical Journal* 108, 2854 (2015).

W. Stephenson, S. Keller, R. Santiago, J. E. Albrecht, P. N. Asare-Okai, S. A. Tenenbaum, M. Zuker and Pan T. X. Li, *Phys. Chem. Chem. Phys.* 16, 906 (2014).

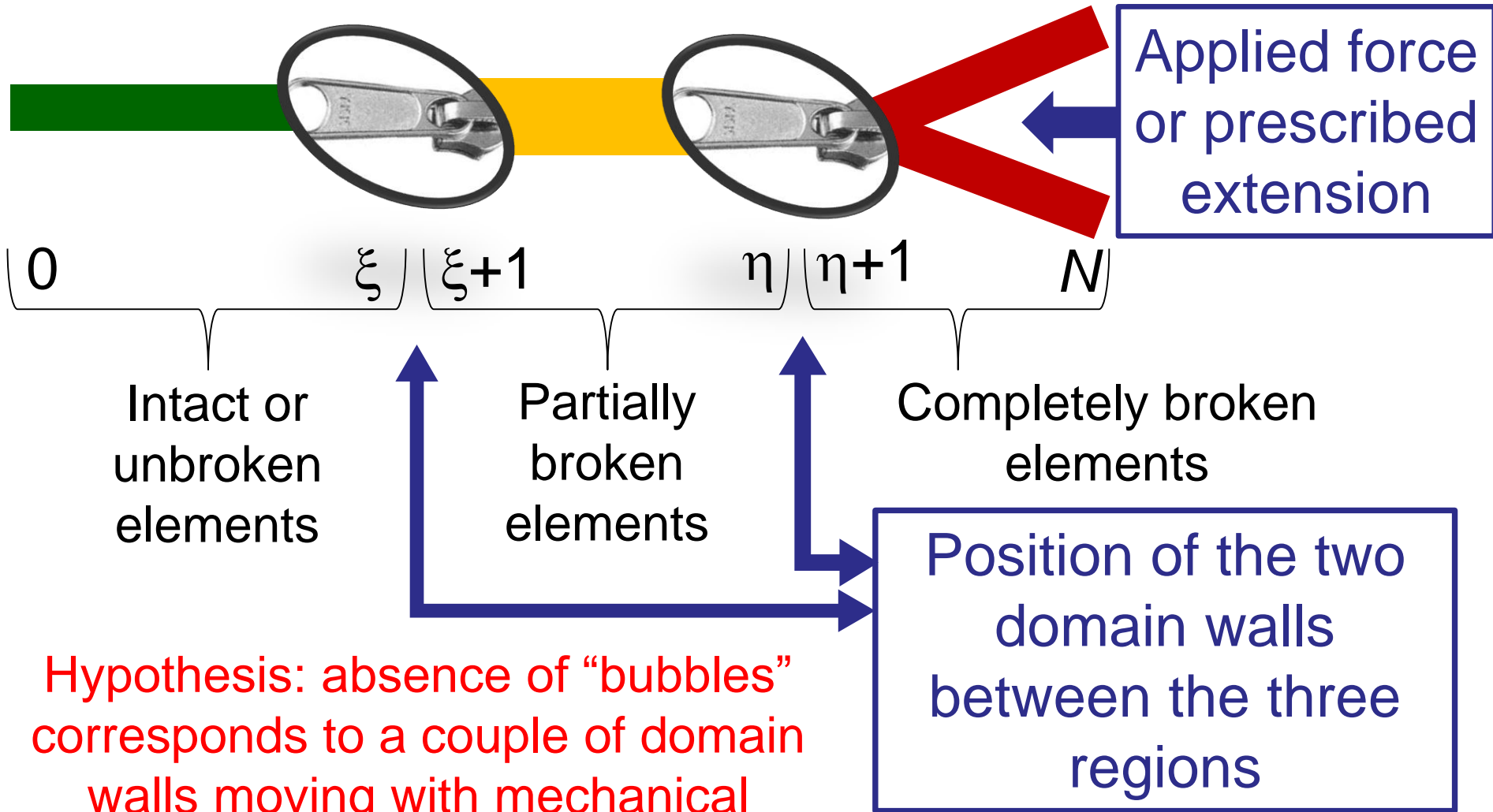


R. B. Wallace, J. Shaer, R. F. Murphy, J. Bonner, T. Hirose, K. Itakura, *Nucleic Acids Res.* 6, 3543 (1979).

Generalization with softening



Hypothesis: extension of the zipper model



Hypothesis: absence of “bubbles” corresponds to a couple of domain walls moving with mechanical actions and temperature

$\alpha = h_e/k, \beta = h_p/k$ Ratios between elastic constants

\vec{y} Vertical positions of the elements

$$\Phi(\vec{y}, \xi, \eta; y_{N+1}) = \frac{1}{2} k \vec{y}^T \mathcal{A}_N^{\xi, \eta}(\alpha, \beta) \vec{y} - k y_{N+1} \vec{v}^T \vec{y} + \frac{1}{2} k y_{N+1}^2 + (N - \xi) \Delta E + (N - \eta) \frac{1}{2} h_p y_b^2$$

Where $\vec{v} = (0, 0, 0, \dots, 0, 1) \in \mathbb{R}^N$ and $\mathcal{A}_N^{\xi, \eta}(\alpha, \beta)$ is a tridiagonal matrix

$$\mathcal{A}_N^{\xi, \eta}(\alpha, \beta) = \begin{bmatrix} a_1 & -1 & 0 & \cdots & 0 \\ -1 & a_2 & -1 & \ddots & \vdots \\ 0 & -1 & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & a_{N-1} & -1 \\ 0 & \cdots & 0 & -1 & a_N \end{bmatrix} \in \mathcal{M}_{N, N}(\mathbb{R})$$

$$\text{with } \begin{cases} a_1 = \dots = a_\xi = 2 + \alpha, \\ a_{1+\xi} = \dots = a_\eta = 2 + \beta, \\ a_{1+\eta} = \dots = a_N = 2. \end{cases}$$

Properties of $\mathcal{A}_N^{\xi, \eta}(\alpha, \beta)$

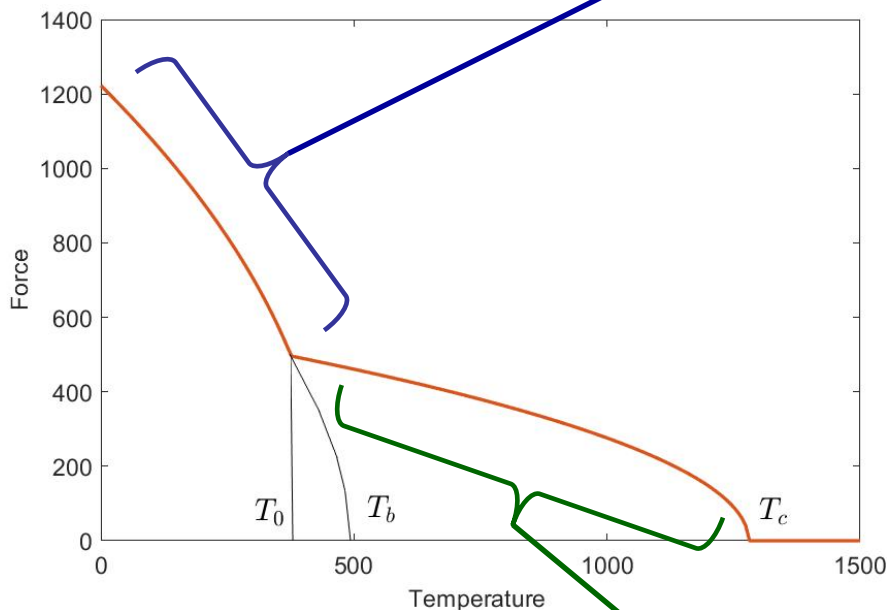
$$\det \left[\mathcal{A}_N^{\xi, \eta}(\alpha, \beta) \right] = (N - \eta + 1) [\mathcal{G}(\beta, \eta - \xi + 1) \mathcal{G}(\alpha, \xi + 1) - \mathcal{G}(\beta, \eta - \xi) \mathcal{G}(\alpha, \xi)] \\ - (N - \eta) [\mathcal{G}(\beta, \eta - \xi) \mathcal{G}(\alpha, \xi + 1) - \mathcal{G}(\beta, \eta - \xi - 1) \mathcal{G}(\alpha, \xi)]$$

$$\mathcal{G}(\gamma, z) = \frac{1}{\sqrt{\gamma^2 + 4\gamma}} \left[\left(\frac{2 + \gamma + \sqrt{\gamma^2 + 4\gamma}}{2} \right)^z - \left(\frac{2 + \gamma - \sqrt{\gamma^2 + 4\gamma}}{2} \right)^z \right]$$

$$1 - \vec{v}^T \left[\mathcal{A}_N^{\xi, \eta}(\alpha, \beta) \right]^{-1} \vec{v} = \frac{\mathcal{G}(\alpha, \xi + 1)}{\det \left[\mathcal{A}_N^{\xi, \eta}(\alpha, \beta) \right]} [\mathcal{G}(\beta, \eta - \xi + 1) - \mathcal{G}(\beta, \eta - \xi)] \\ - \frac{\mathcal{G}(\alpha, \xi)}{\det \left[\mathcal{A}_N^{\xi, \eta}(\alpha, \beta) \right]} [\mathcal{G}(\beta, \eta - \xi) - \mathcal{G}(\beta, \eta - \xi - 1)]$$

Force-temperature behavior

$$T < T_0 \Rightarrow \langle \mathcal{F} \rangle_{as} = \sqrt{\frac{\beta\delta - \frac{1}{2} \log \alpha_0 + \varphi}{\delta}} = \sqrt{\frac{2\Delta E}{ky_b^2} + \frac{h_p}{k} \sqrt{1 - \frac{T}{T_b}}}$$



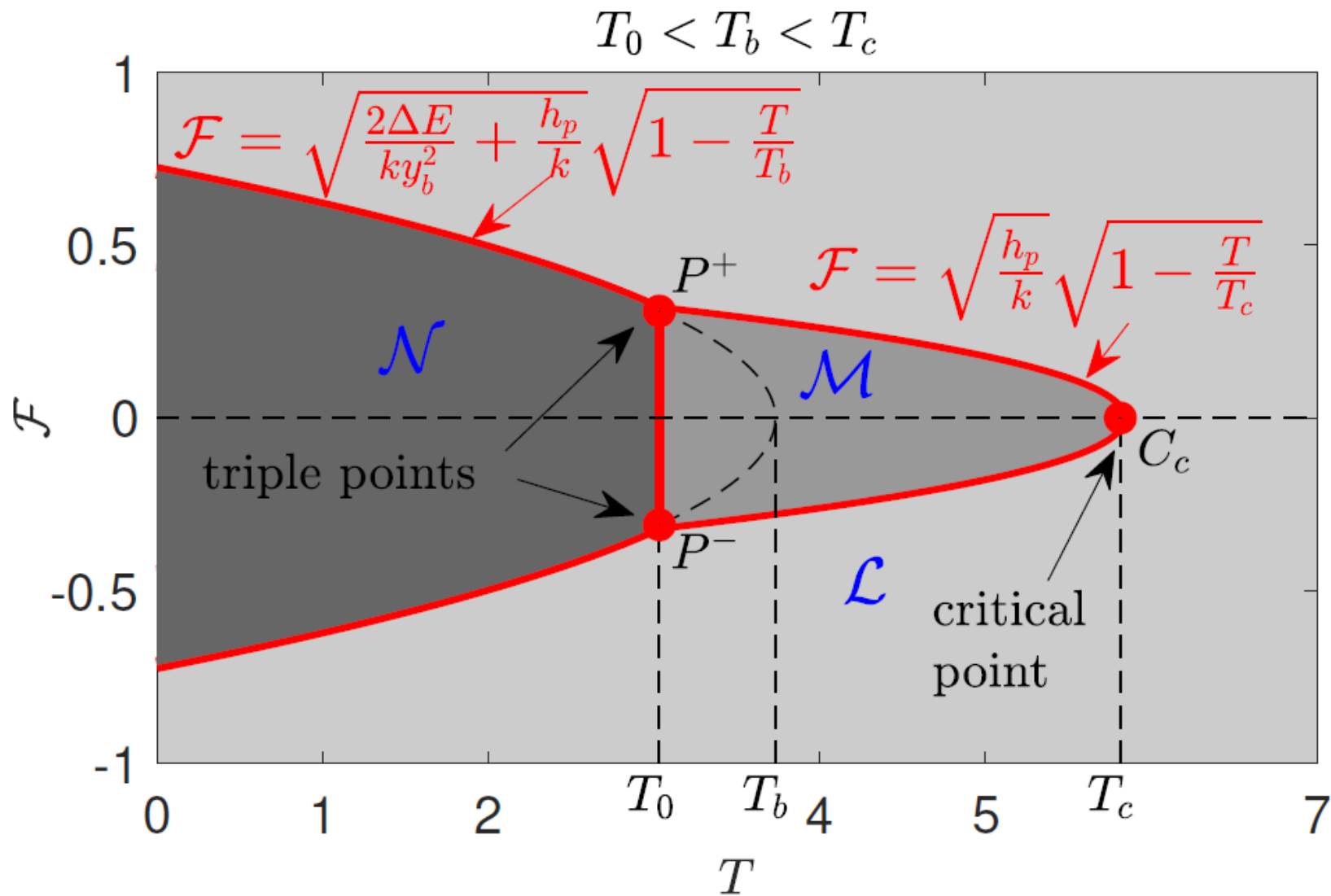
$$T_b = \frac{2\Delta E + h_p y_b^2}{K_B \log \alpha_0} = \frac{2\Delta E + h_p y_b^2}{K_B \log \frac{2+\alpha+\sqrt{\alpha^2+4\alpha}}{2}}$$

$$T_0 = \frac{2\Delta E}{K_B \log \frac{\alpha_0}{\beta_0}}$$

$$T_c = \frac{h_p y_b^2}{K_B \log \beta_0} = \frac{h_p y_b^2}{K_B \log \frac{2+\beta+\sqrt{\beta^2+4\beta}}{2}}$$

$$T > T_0 \Rightarrow \langle \mathcal{F} \rangle_{as} = \sqrt{\frac{\beta\delta - \frac{1}{2} \log \beta_0}{\delta}} = \sqrt{\frac{h_p}{k} \sqrt{1 - \frac{T}{T_c}}}$$

Phase diagram

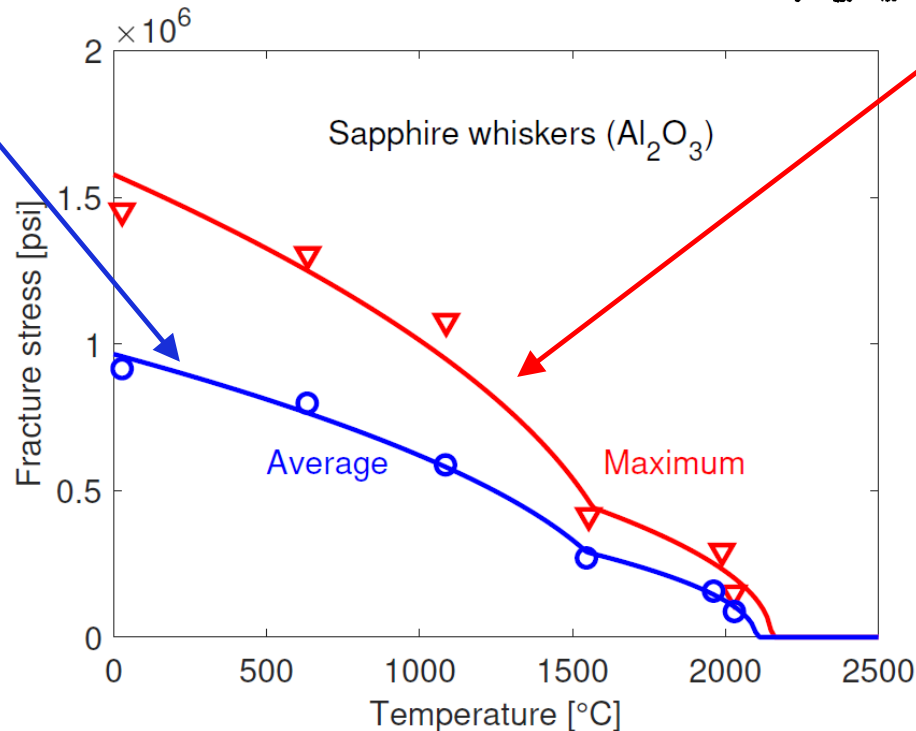
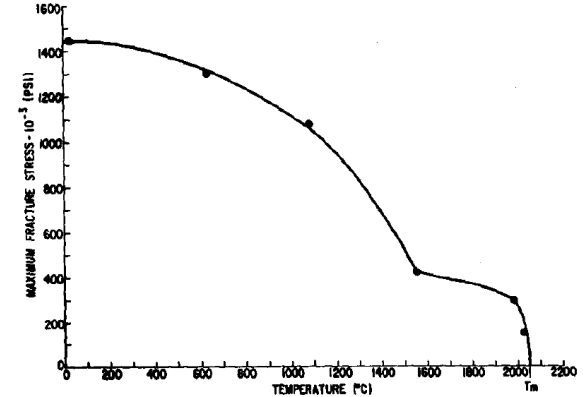
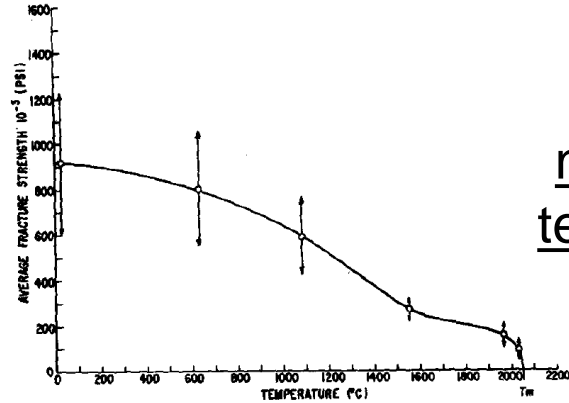


Mechanical Behavior of Sapphire Whiskers at Elevated Temperatures

S. S. BRENNER*

General Electric Research Laboratory, Schenectady, New York

Dislocation
nucleation at high
temperature before
cracking

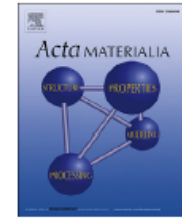




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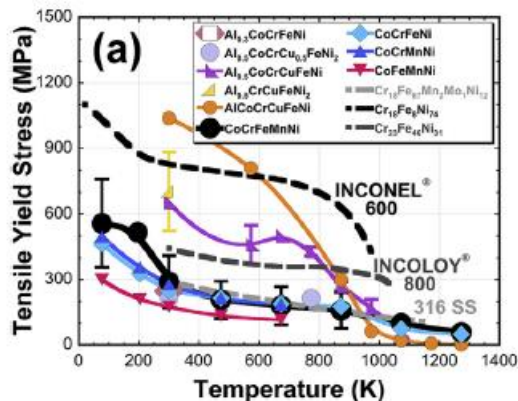
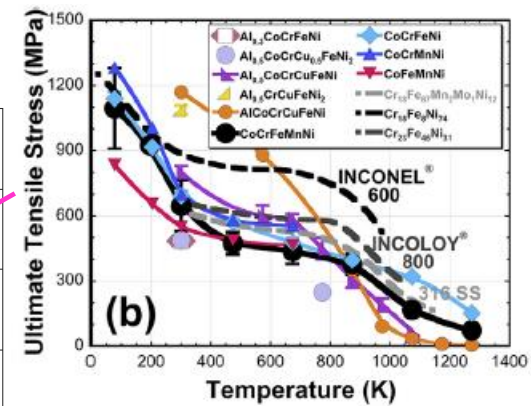
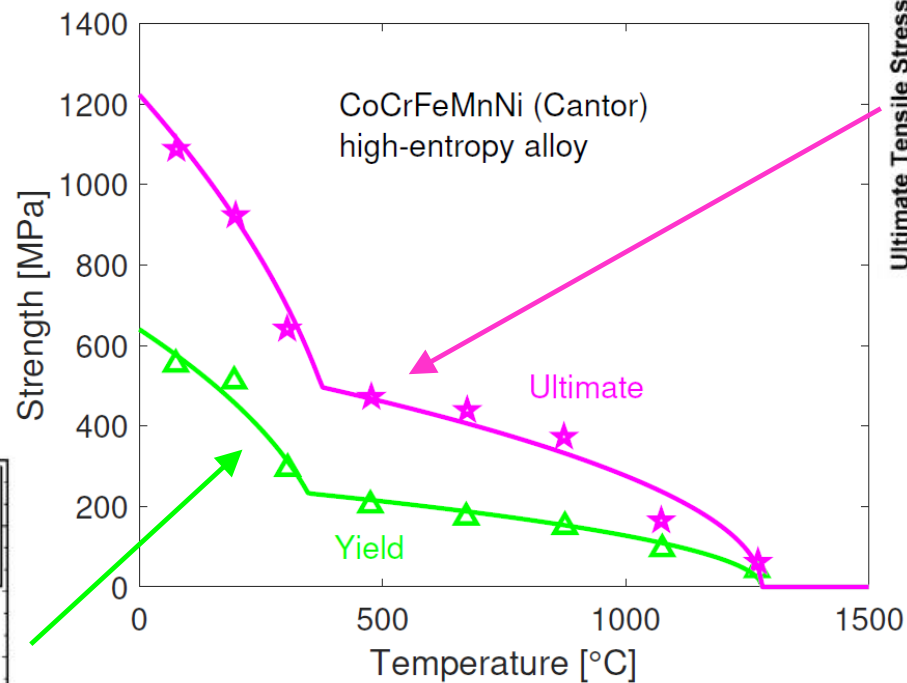
journal homepage: www.elsevier.com/locate/actamat

By invitation only: overview article

A critical review of high entropy alloys and related concepts

D.B. Miracle ^{a,*}, O.N. Senkov ^{a,b}

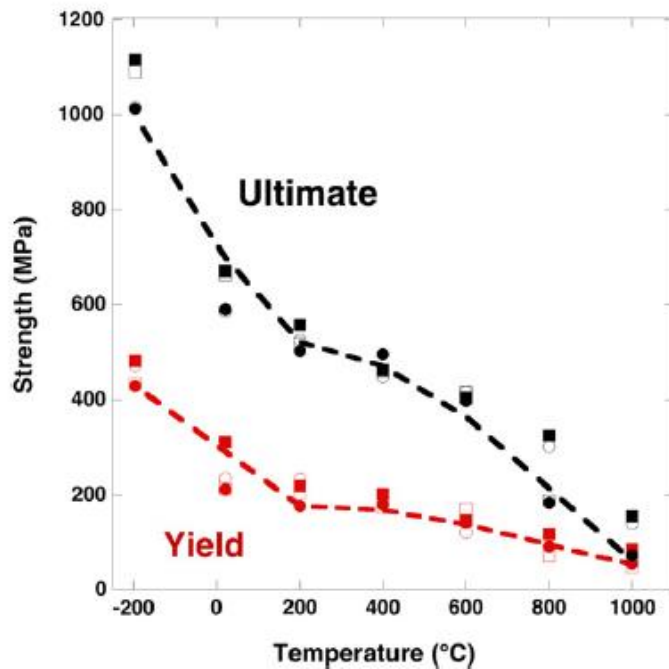
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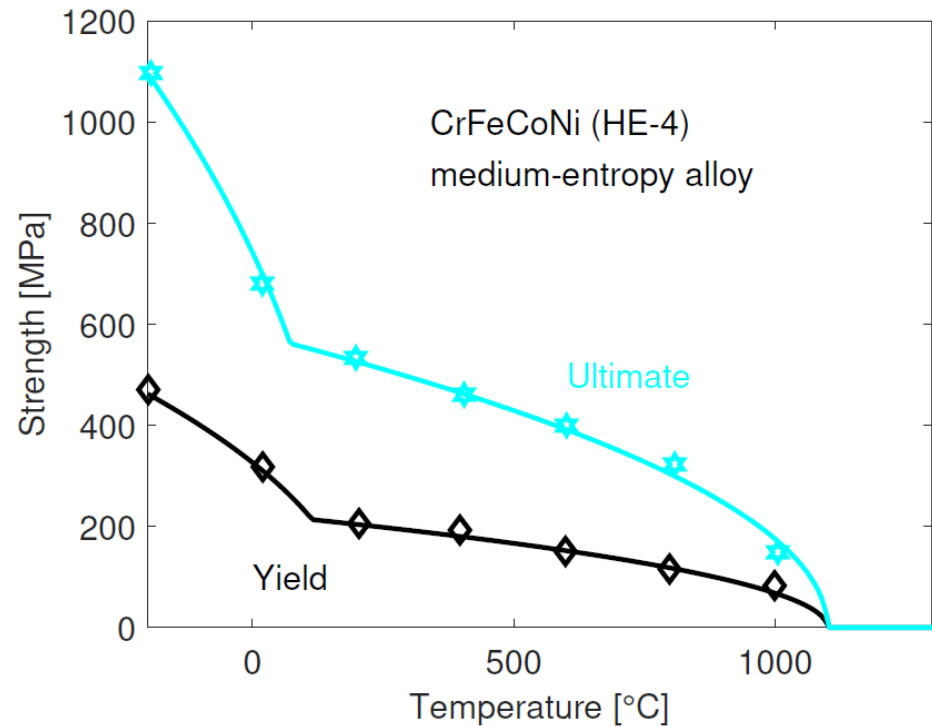


Tensile properties of high- and medium-entropy alloys

A. Gali^{a,b}, E.P. George^{a,b,*}



Experimental results



Comparison with theory

Conclusions

- The combination of **statistical mechanics** and **nanomechanics** allows for studying the behavior of systems in large temperature intervals and over a wide range of sizes (from the nanoscale to the macroscale).
- Moreover, we can approach problems pertaining to rather **different topics**, spanning soft matter, biophysics, mechanics of adhesion, fracture mechanics, material science and so on.
- To conclude, some perspective concerns the study of the **dynamics** (out-of-equilibrium statistical mechanics) and the effect of the **heterogeneity** in systems with microinstabilities.

THANK YOU FOR YOUR ATTENTION !

Main publications:

JCP 137, 244907 (2012)
JCP 136, 154906 (2012)
PRE 87, 032705 (2013)
Phys. A: Stat. Mech. Appl. 395, 154 (2014)
PRL 113, 255501 (2014)
EPJE 38, 44 (2015)
Eur. J. Mech. A/Sol. 60, 145 (2016)
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Soft Matter 13, 6877-6893 (2017)
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JCP 149, 054901 (2018)
PRE (Editors' Suggestion) 98, 052146 (2018)
EPJB 92, 174 (2019)
Inventions 4, 19 (2019)
Phys. Lett. A, 10.1016/j.physleta.2019.126124 (2019)