Nonequilibrium Thermodynamics and STZ's

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KITP, Glasses-10
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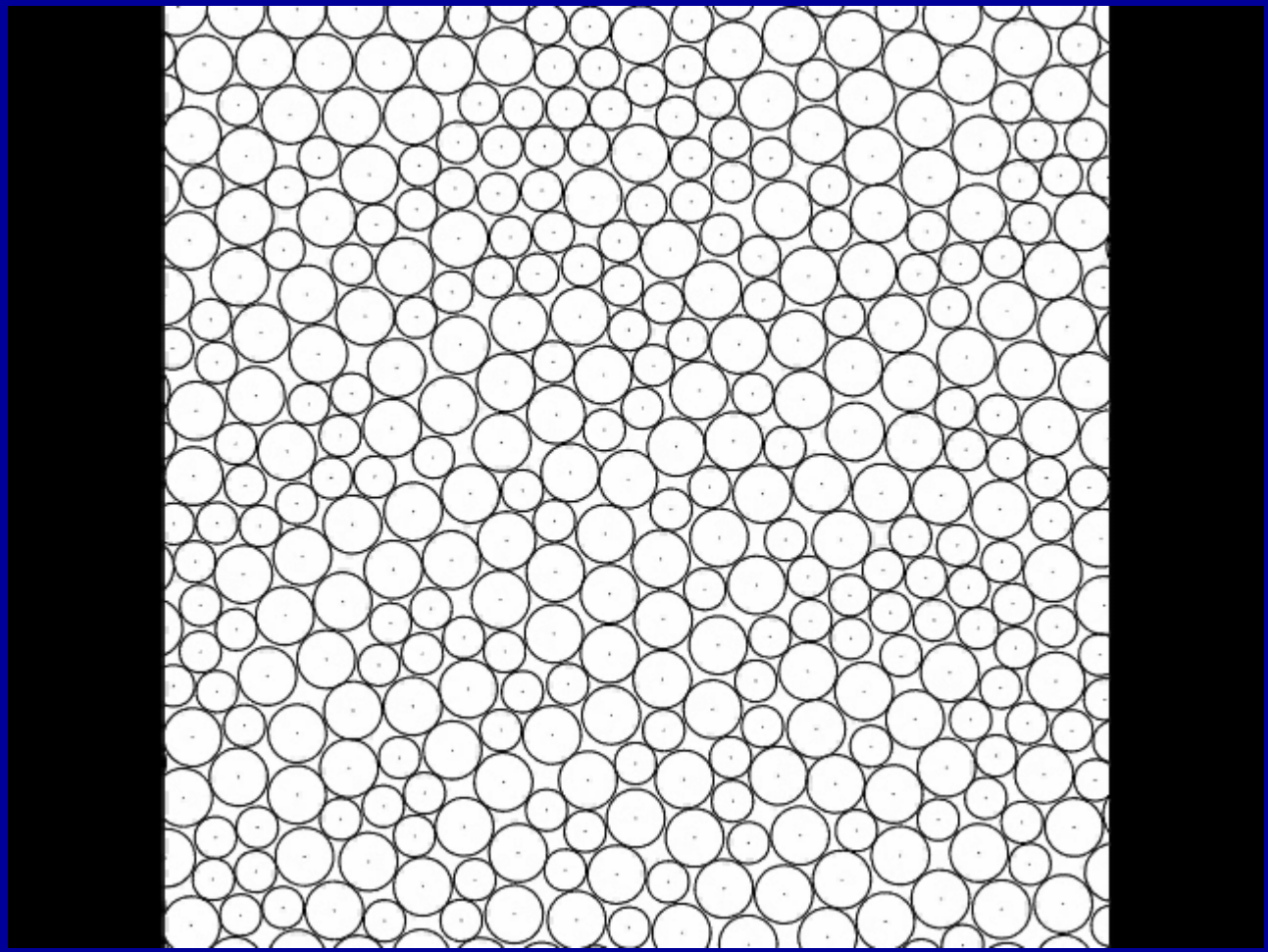
In collaboration with

Eran Bouchbinder (Thermodynamics, etc..)

Michael Falk (STZ theory from the beginning)

M. Lisa Manning (Glass deformation, shear bands)



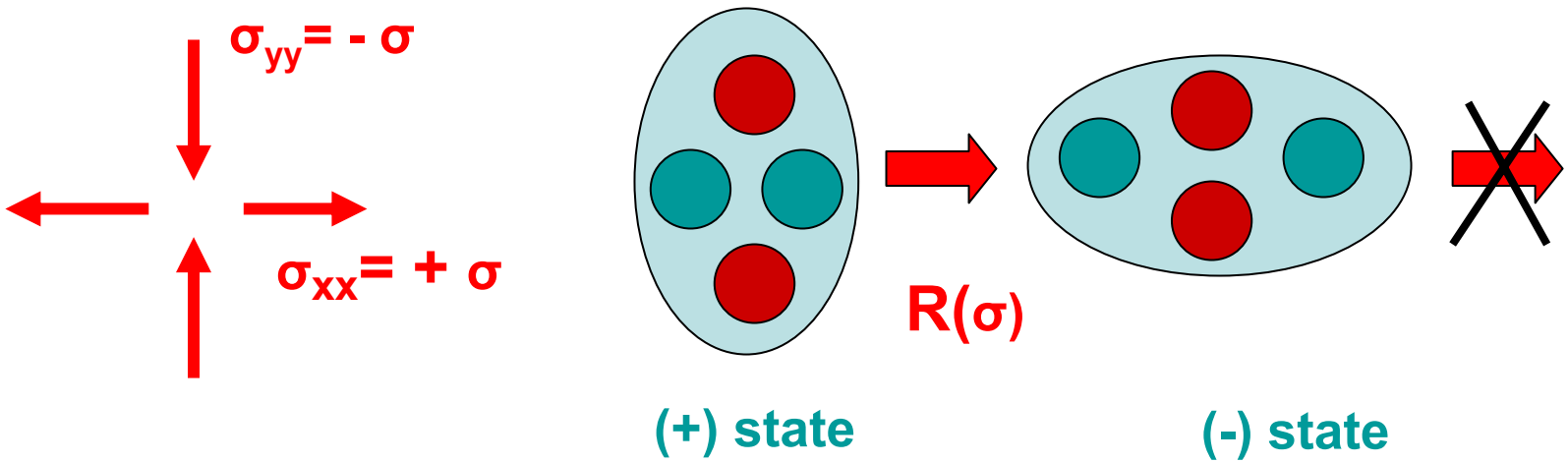
T. Haxton and A. Liu: MD simulation of 2D glass. The temperature is nonzero but is below the glass transition; the shear rate is constant but very small on the molecular time scale.

Basic Assumptions of STZ Theory

- Starting point: Elastic solid + flow defects
- High-frequency thermal and/or mechanically generated noise
- STZ transitions: Rare, localized, irreversible, molecular rearrangements
- STZ's are ephemeral, more like nucleating droplets in a supercooled vapor than defects with fixed positions.

Simple Two-State STZ Model

For simplicity, assume that the deviatoric (shear) stress σ_{ij} has a fixed orientation, and that the STZ's are two-state systems aligned along the same axes.



R(σ) is proportional to the rate at which (+) → (-) transitions occur in response to the stress s. Reverse (-) →(+) transitions occur at rate R(- σ).

Plastic strain rate = rate of volume-conserving deformation:

$$\tau_0 \dot{\varepsilon}^{pl} = v_0 \left[R(\sigma) n_- - R(-\sigma) n_+ \right]$$

$n_\pm$ = number of ± STZ's per unit volume

τ_0 = characteristic time scale (~ molecular vibration period)

v_0 ~ molecular volume ~ n_∞^{-1}

Equation of motion for $n_\pm$:

$$\tau_0 \dot{n}_\pm = R(\pm\sigma) n_\mp - R(\mp\sigma) n_\pm + \Gamma(\sigma) \left(\frac{1}{2} n_{eq} - n_\pm \right)$$

$\Gamma(\sigma)/\tau_0 \propto$ noise strength, i.e. attempt frequency

$n_{eq} \approx n_\infty e^{-1/\chi}$ = equilibrated STZ density; $\chi = k_B T_{eff} / e_Z$ = scaled effective temperature

$\frac{\Gamma(\sigma)}{2\tau_0} n_{eq}$ = STZ creation rate; $\frac{\Gamma(\sigma)}{\tau_0} n_\pm$ = STZ annihilation rate

STZ Order Parameters
(Internal State Variables)

$$\frac{n_+ + n_-}{n_\infty} = \frac{n_{STZ}}{n_\infty} = \Lambda =$$ scaled, scalar density of STZ's $\propto e^{-1/\chi}$

$$\frac{n_+ - n_-}{n_\infty} = m\,\Lambda =$$ orientational bias of STZ's

$m \rightarrow m_{ij} =$ traceless, symmetric tensor, consistent with volume conserving plasticity

For simplicity, ignore tensorial features throughout this presentation. That is, assume that the orientation of the stress remains fixed. It is easy to fix this for more general applications.

Nonequilibrium Thermodynamics: The Effective Disorder Temperature

E. Bouchbinder and J.S. Langer, Phys.Rev. E 80, 031131, 031132, (2009).

During irreversible plastic deformation of an amorphous solid, molecular rearrangements drive the slow configurational degrees of freedom (inherent structures) out of equilibrium with the heat bath.

Because those degrees of freedom maximize an entropy, say S_C, which is a function of the configurational energy U_C, the state of disorder is characterized by a temperature.

$$\chi = \frac{\partial U_C}{\partial S_C}$$

Quasi-Thermodynamic Hypothesis

- Under steady-state conditions, i.e. constant strain rate, the effective temperature $\mathfrak{m}$ plays a role directly analogous to that of the thermal temperature T.

- Extensive quantities such as the potential energy, the density, the density of liquidlike sites in a-Si, etc. obey equations of state in which $\mathfrak{m}$ appears as an independent variable.

Effective Temperature Thermodynamics

Separable Configurational + Kinetic/Vibrational Subsystems

Total Energy $\cong H_C + H_K$

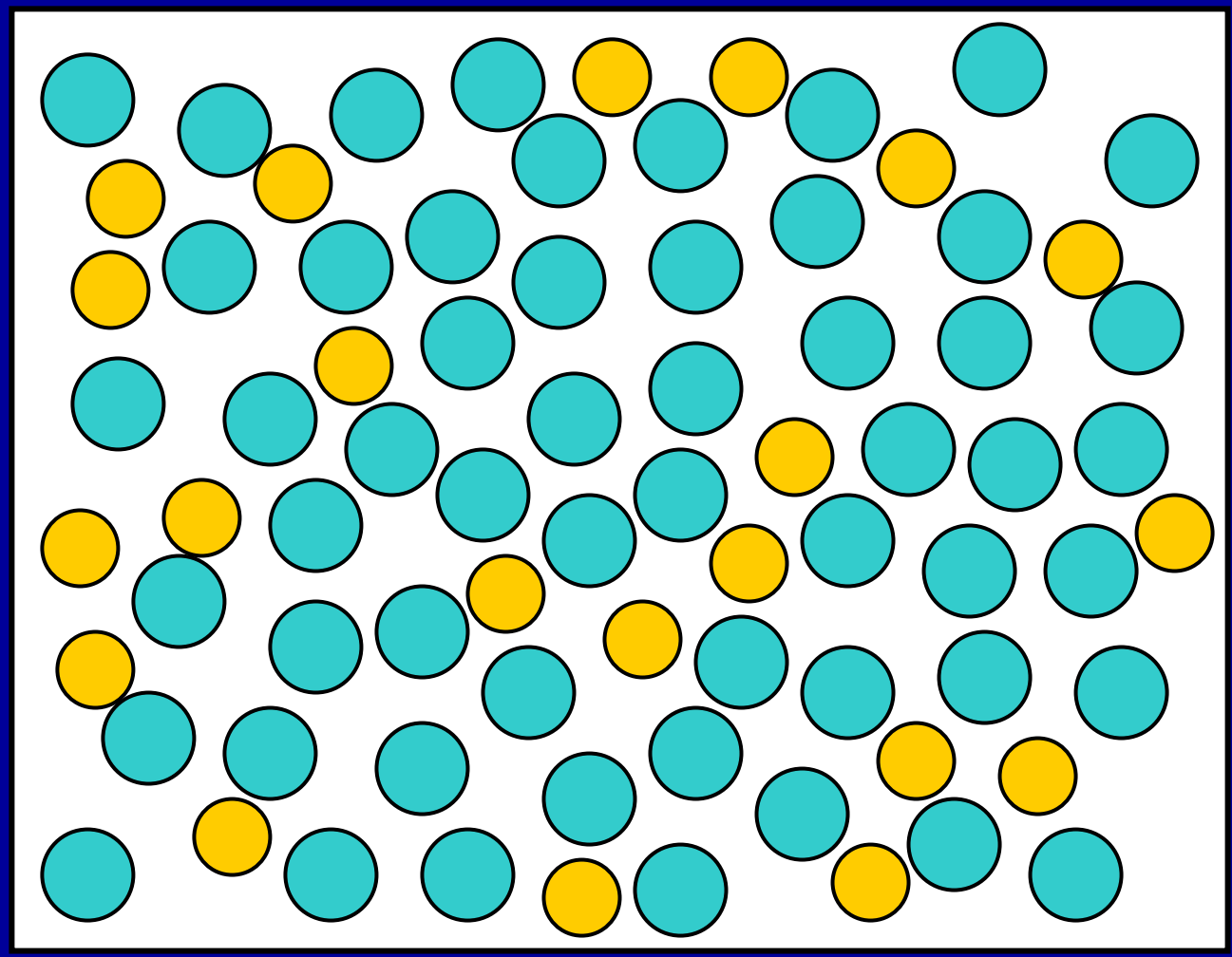
$H_C = H_C\{r_v\}$ = configurational energy of the ■'th inherent-structure

$\{r_v\}$ = set of molecular positions at the potential-energy minimum for the ■'th inherent-structure

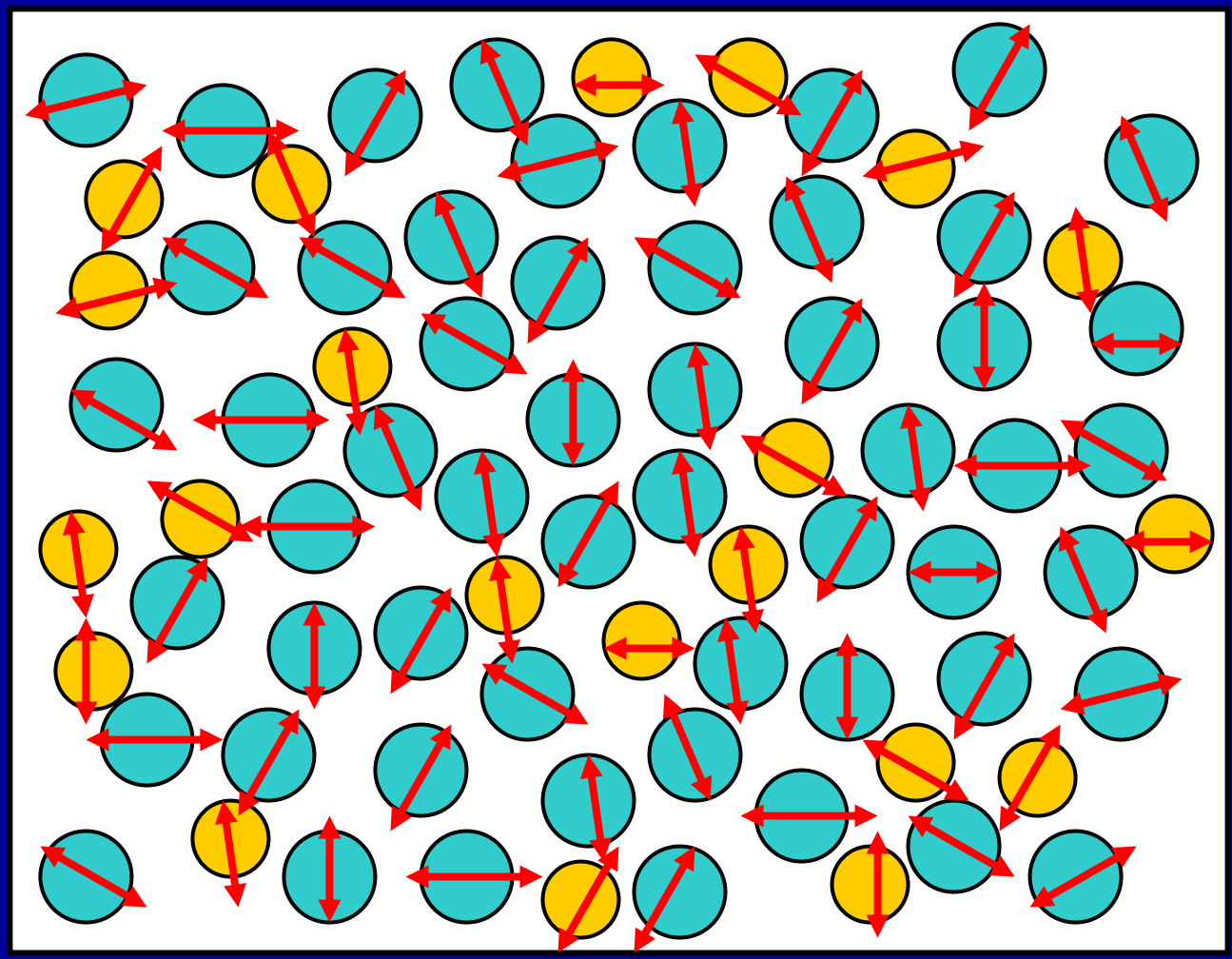
$H_K = H_K\{p, \delta r_v\}$ = kinetic energy + harmonic potential energy for small excursions from configurational minima.

This subsystem serves as the thermal reservoir at temperature $\theta = k_B T$.

Assume weak coupling between these two subsystems.

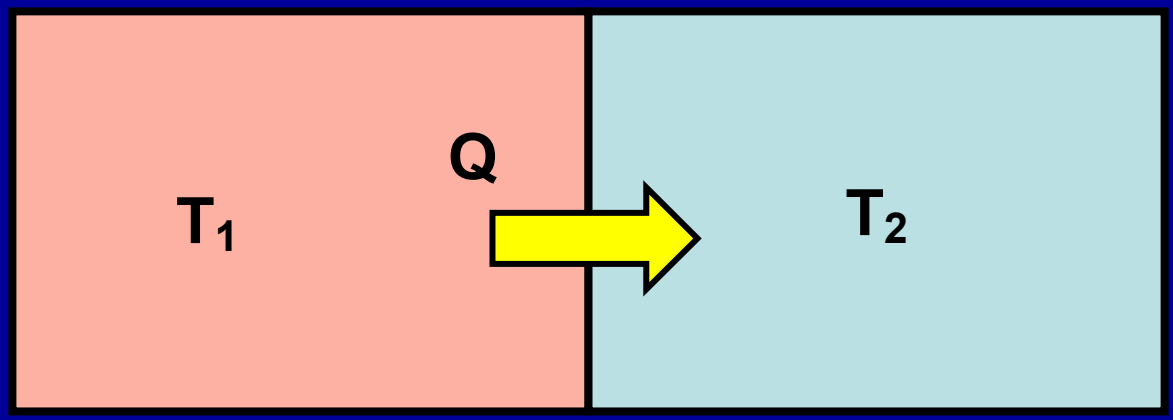


Inherent structure with molecules fixed in a mechanically stable configuration



Kinetic/vibrational degrees of freedom superimposed on the inherent structure. In a glassy system, these rapid motions are only weakly coupled to the slow configurational transitions from one inherent structure to another.

Textbook analogy



Spatially separated subsystems in weak thermal contact with each other:

If $T_1 > T_2$, then heat Q flowing from the hotter to the cooler subsystem increases the entropy of the system as a whole.

$$\dot{S}_{tot} = \frac{\dot{U}_1}{T_1} + \frac{\dot{U}_2}{T_2} = \dot{U}_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0$$

Therefore $Q = -\dot{U}_1 = A(T_1 - T_2); \quad A \geq 0$

Total internal energy: $U_{tot} = U_C(S_C, \{\Lambda_\alpha\}) + U_K(S_K)$

S_C and S_K are the configurational and kinetic/vibrational entropies.

$\{\Lambda_\alpha\}$ denotes a set of internal variables, e.g. the number of STZ's or other kinds of defects.

The effective and thermal temperatures, in energy units, are:

$$\chi = \frac{\partial U_C}{\partial S_C}; \quad \theta = \frac{\partial U_K}{\partial S_K}$$

First law of thermodynamics: $V\sigma : \dot{\varepsilon}^{pl} = \dot{U}_{tot} = \chi \dot{S}_C + \theta \dot{S}_K + \sum_\alpha \frac{\partial U_C}{\partial \Lambda_\alpha} \dot{\Lambda}_\alpha$

σ = shear stress; V = volume.

Second Law of Thermodynamics

Various "fundamental" statements: Are they equivalent?

Cannot make a perpetual-motion machine.

Kelvin-Planck + Clausius: Cannot convert heat directly into work.

Clausius-Duhem: Non-negative rate of entropy production.
But – what is meant by "entropy" in a nonequilibrium situation?

Coleman-Noll (1963): Axiomatic approach. The C-D inequality *defines* entropy and temperature. *But* – How do we make contact with statistical definitions of entropy? What happens if there are two temperatures?

In order to construct an effective-temperature theory of plasticity, we (Bouchbinder and JSL) have had to address these basic issues.

Second Law of Thermodynamics, continued

Gibbs + physicists: The statistically defined entropy of an isolated system is non-decreasing. *But* – how do we define/compute the entropy for a nonequilibrium system? We need to consider internal degrees of freedom and their variations.

Total internal energy as a function of entropy:

$$U_{total} = U_C(S_C, \{\Lambda_\alpha\}) + U_K(S_K)$$

The inverse of this relation is the microcanonical expression for the *constrained* entropy as a function of U and Λ. (Count states at fixed U and Λ.)

$$S_{total} = S_C(U_C, \{\Lambda_\alpha\}) + S_K(U_K)$$

For this to be the non-decreasing entropy to be used in the 2nd law, the internal variables Λ (like U) must be *extensive* quantities. Then the constrained entropy S(U,Λ) is equal to S in the thermodynamic limit.

Application of the Second Law

$$\dot{S}_C + \dot{S}_K \geq 0$$

Use the first law to eliminate $\dot{S}_C$. The result is:

$$(\chi - \theta)\dot{S}_K + W\left(\dot{\varepsilon}^{pl}, \{\dot{\Lambda}_\alpha\}\right) \geq 0 \quad \text{where} \quad W\left(\dot{\varepsilon}^{pl}, \{\dot{\Lambda}_\alpha\}\right) = V\sigma : \dot{\varepsilon}^{pl} - \sum_\alpha \frac{\partial U_C}{\partial \Lambda_\alpha}\dot{\Lambda}_\alpha$$

These two terms must separately be non-negative.

$$(\chi - \theta)\dot{S}_K \geq 0 \quad \Rightarrow \quad \theta \dot{S}_K = A(\chi - \theta), \quad A \geq 0.$$

Heat flows from the C to the K subsystem if $\chi > \theta$.

$W\left(\dot{\varepsilon}^{pl}, \{\dot{\Lambda}_\alpha\}\right) \geq 0$ constrains the equations of motion for the internal variables. (~ Clausius-Duhem)

With these results, the first law becomes an equation of motion for the effective temperature:

$$\chi \dot{S}_C = W\left(\dot{\varepsilon}^{pl}, \{\dot{\Lambda}_\alpha\}\right) - A(\chi - \theta) \cong C_V{}^{eff}\,\dot{\chi}$$

Ultra-simple example: No driving stress or strain rate
Λ = (number of STZ's)/ N

$$U_C = N\Lambda e_Z + U_1(S_1) = N\Lambda e_Z + U_1[S_C - S_0(\Lambda)]$$

$$S_C = S_0(\Lambda) + S_1(U_1); \quad S_0(\Lambda) = -\Lambda \ln \Lambda + \Lambda$$

U_1 and S_1 = energy and entropy of everything except the STZ's.

e_Z = STZ formation energy

$$W = -\frac{\partial U_C}{\partial \Lambda}\dot{\Lambda} = -\frac{\partial F_Z}{\partial \Lambda}\dot{\Lambda} \geq 0; \quad F_Z = e_Z \Lambda - \chi S_0(\Lambda)$$ = STZ free energy

2nd law requires that $\dot{\Lambda} \propto -\frac{\partial F_Z}{\partial \Lambda} = 0$ at $\Lambda = \Lambda^{eq} \propto exp\left(-\frac{e_Z}{\chi}\right)$

We have *derived* a Clausius-Duhem inequality from statistical first principles. The 2nd law simply tells us that the system goes downhill in free energy. No surprises here – except that $S_0(\Lambda)$ is essential – and is unconventional in the solid mechanics literature.

A short summary of where we go from here:

This situation becomes very much more interesting when the system is deforming under the influence of an external stress, and when the dynamics of the orientational variable m is included.

The second law no longer has a variational interpretation – there is no free-energy minimization principle other than for Λ relaxation. The 2nd law (entropy production) tells us what to use for the noise strength $\Gamma(\sigma)$. (Pechenik)

The resulting equation of motion for m has a jamming-unjamming transition at a dynamical yield stress σ_y. Below the glass transition, for $\sigma < \sigma_y$, $m \rightarrow 1$, i.e. all the existing STZ's are aligned with the stress, and there is no flow. At higher temperatures, the m dynamics predicts a smooth transition from thermally assisted viscosity to "superplasticity" with increasing stress.

STZ Constitutive Relations

$$\dot{\varepsilon}^{pl} = \Lambda \Psi(\sigma, \chi, \theta, \Lambda, m)$$

STZ density

dynamic response factor

This relation must be supplemented by equations of motion for χ, Λ, and m. The Λ equation tells us that

$$\Lambda \rightarrow \Lambda_{ss} \propto exp\left(-\frac{e_Z}{\chi}\right)$$

The m equation tells us that $m \rightarrow m_{ss}(\sigma,\theta)$. In many cases, these relaxation mechanisms are fast relative to plastic response rates; and the constitutive relation takes the form:

$$\dot{\varepsilon}^{pl} = exp\left(-\frac{e_Z}{\chi}\right) \Psi(\sigma,\theta)$$

Equation of motion for χ : Start with 1st law.

$$\chi \dot{S}_C \cong C_V{}^{eff} \dot{\chi} = W\left(\dot{\varepsilon}^{pl}, \{\dot{\Lambda}_\alpha\}\right) - A(\chi - \theta)$$

Heat production

Heat flow to the reservoir (aging)

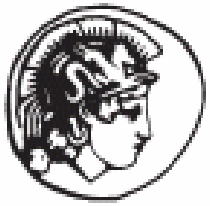
becomes: $c_0 \dot{\chi} \propto e^{-1/\chi} \Gamma(\sigma) \left(1 - \frac{\chi}{\chi_{ss}(\dot{\varepsilon}^{pl})}\right) + \kappa e^{-\beta/\chi} \rho(\theta) \left(1 - \frac{\chi}{\theta}\right)$

Heat generated by deformation drives χ toward steady state χ_{ss}

Strain-rate dependent χ_{ss} → constant at small strain rates

Thermally induced aging Note β.

STZ Analysis of Deformation in Bulk Metallic Glass, Vitreloy 1



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Deformation behavior of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass over a wide range of strain-rates and temperatures

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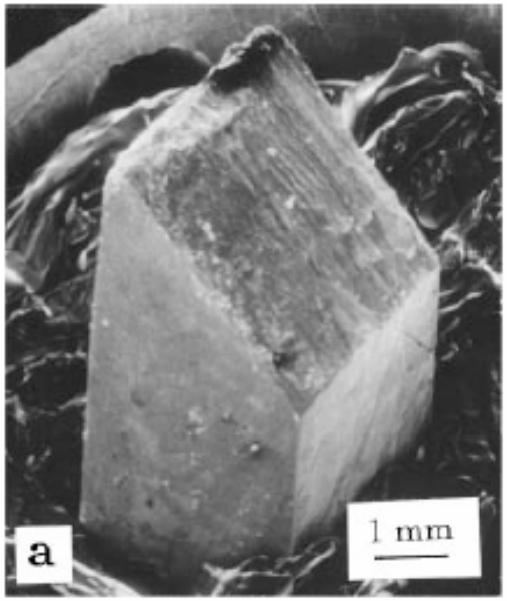
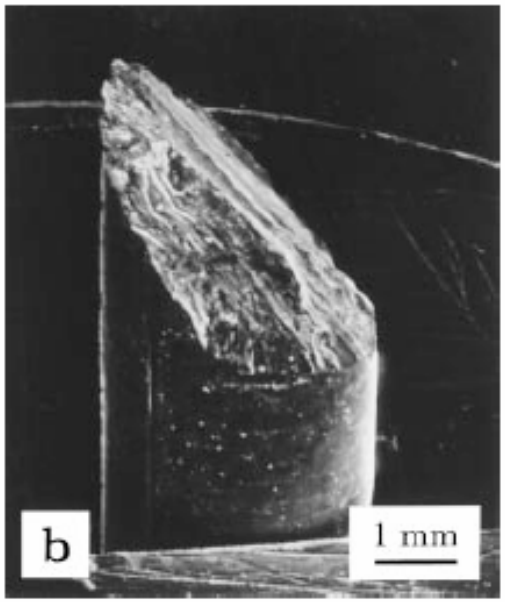
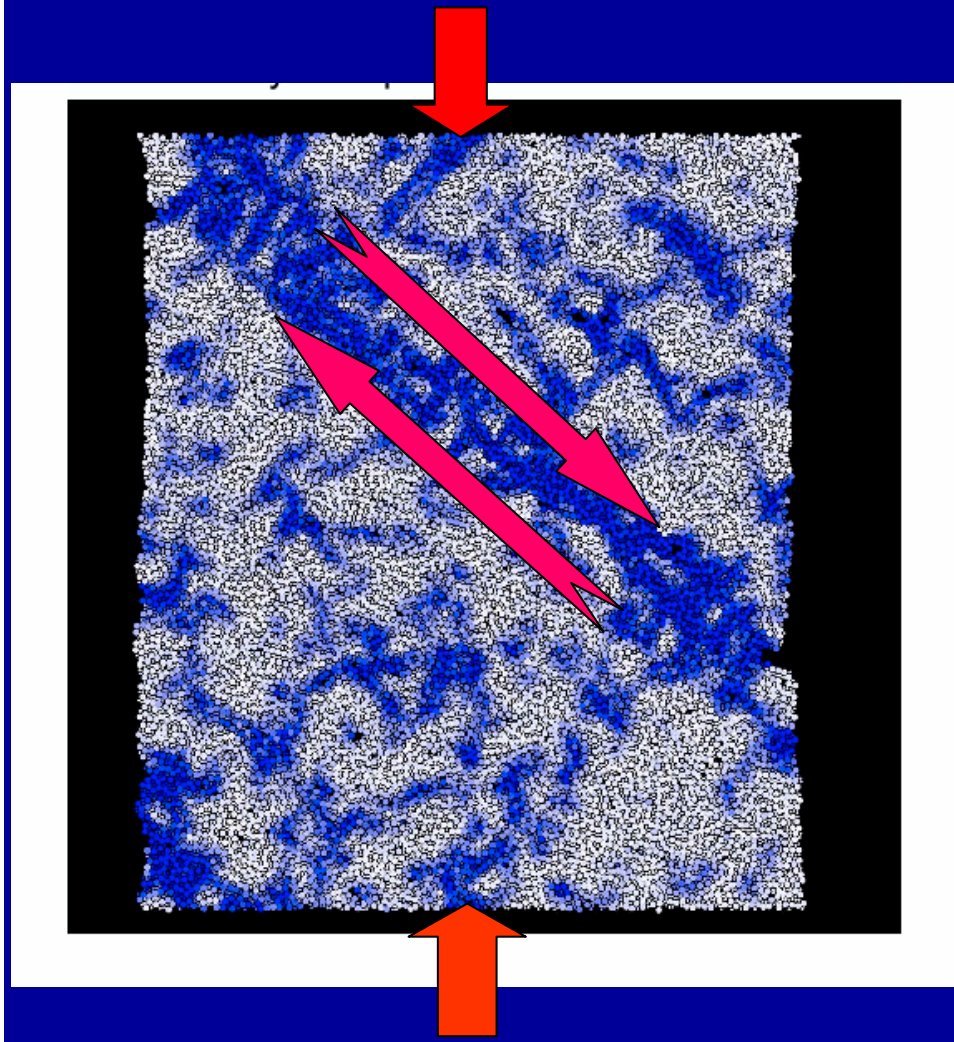
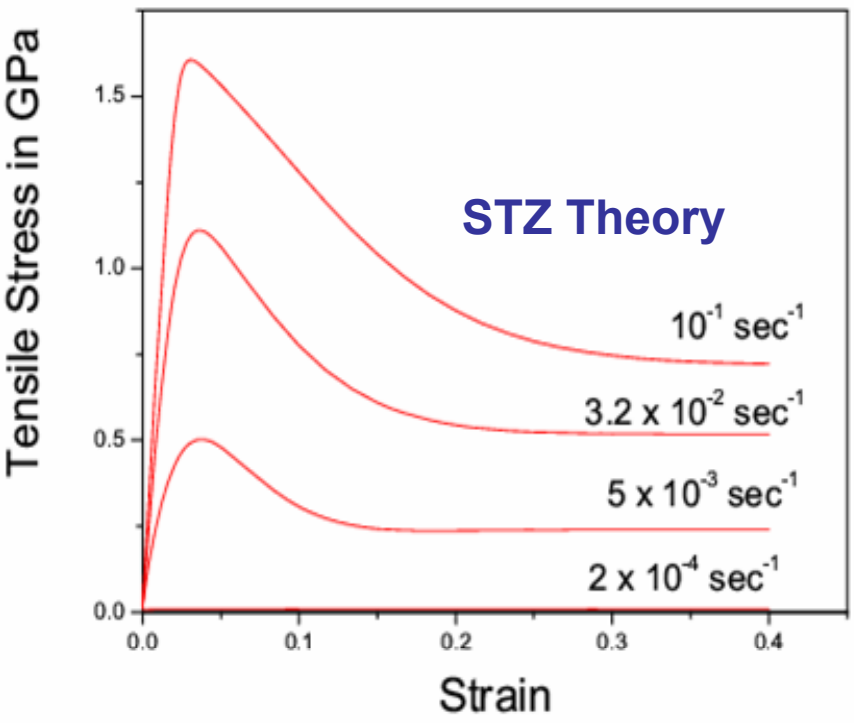


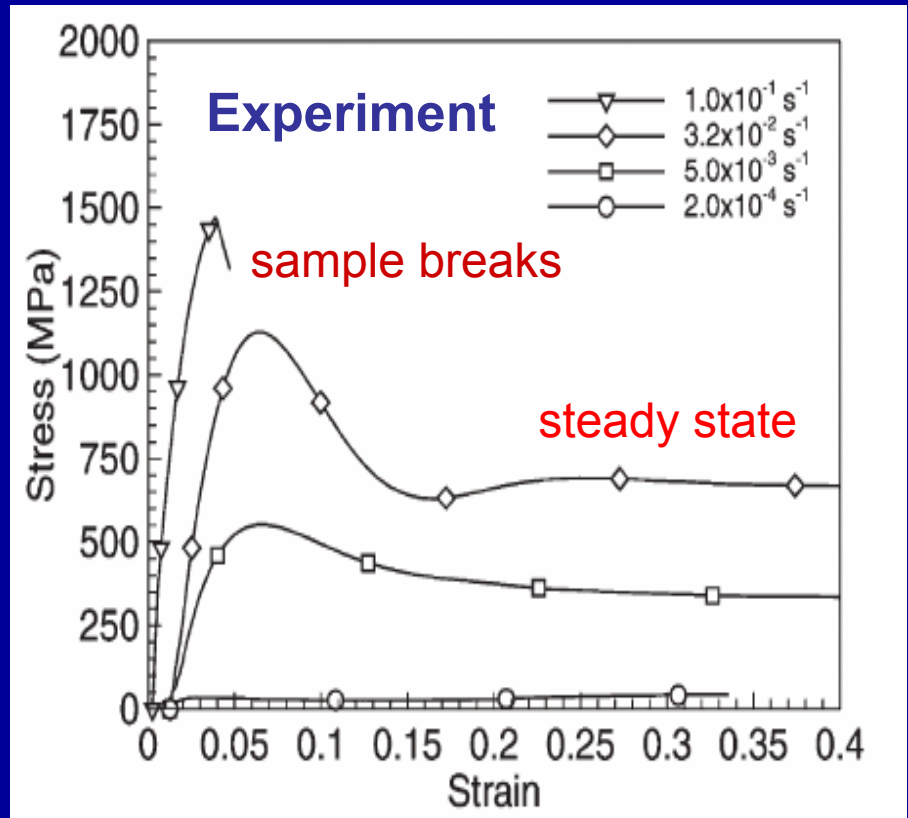


W.Johnson et al, Bulk Metallic Glass



M. Falk, MD Simulation

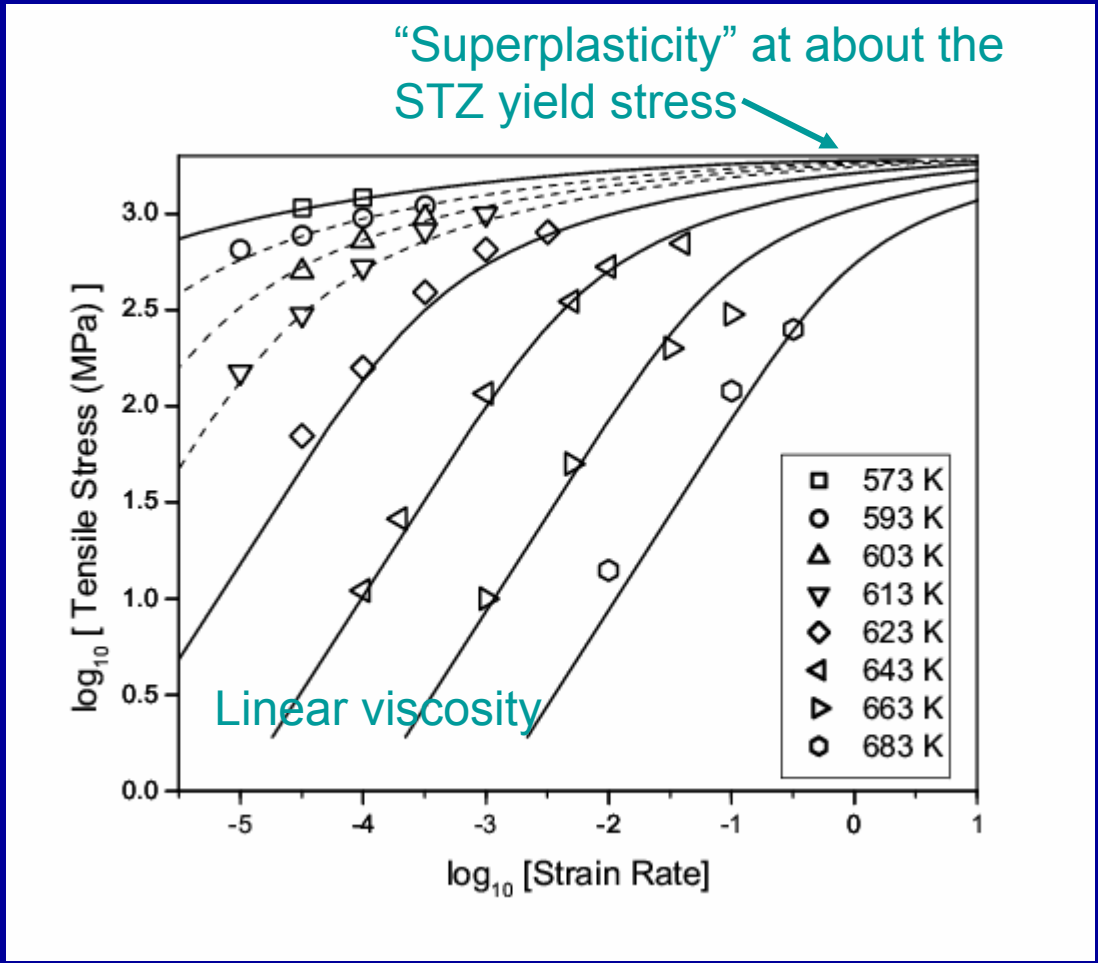




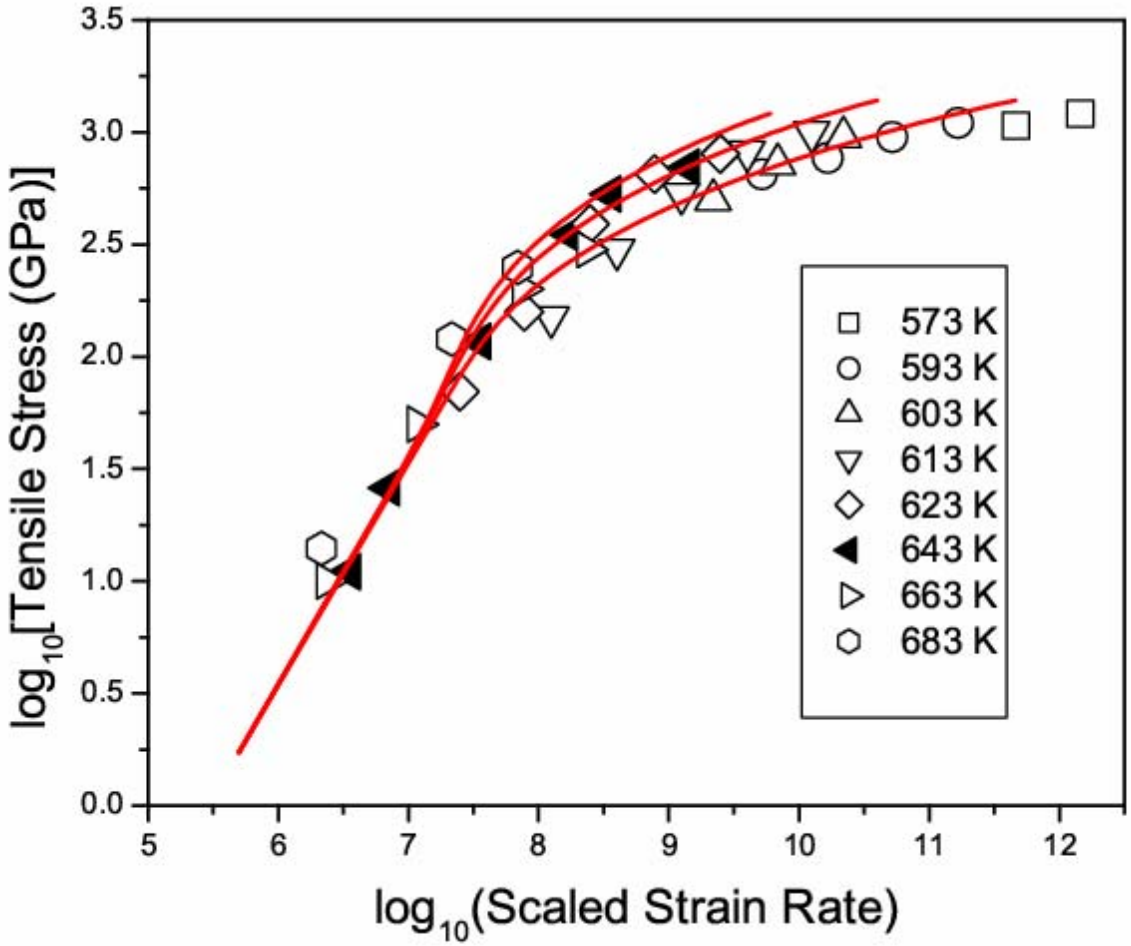
Comparison between STZ theory and experiment for transient behavior at different constant strain rates

T = 643 K

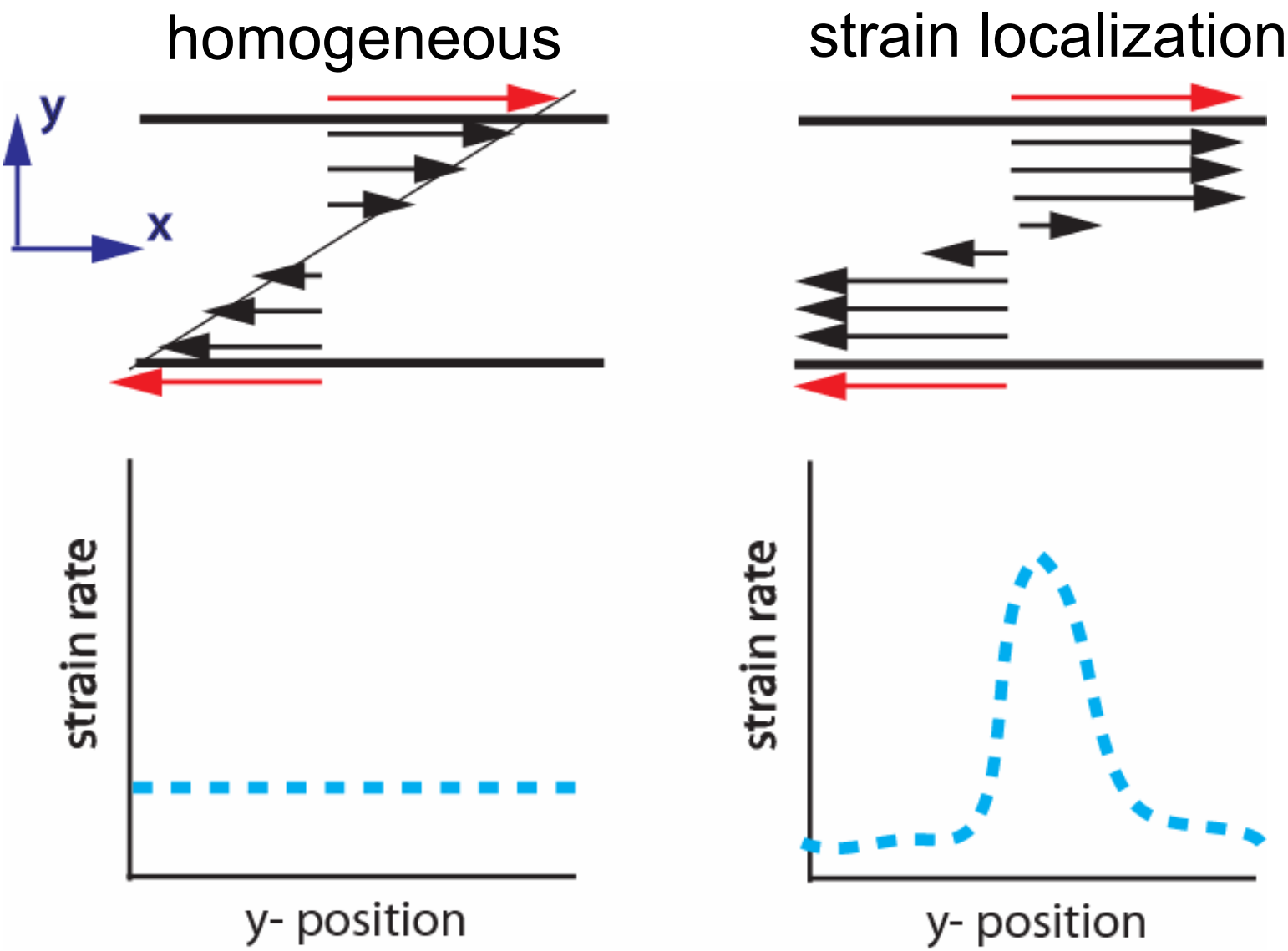
STZ fit to data for stress versus steady-state strain-rate.



Theoretical fit to data for stress as a function of steady-state strain rate x Newtonian viscosity



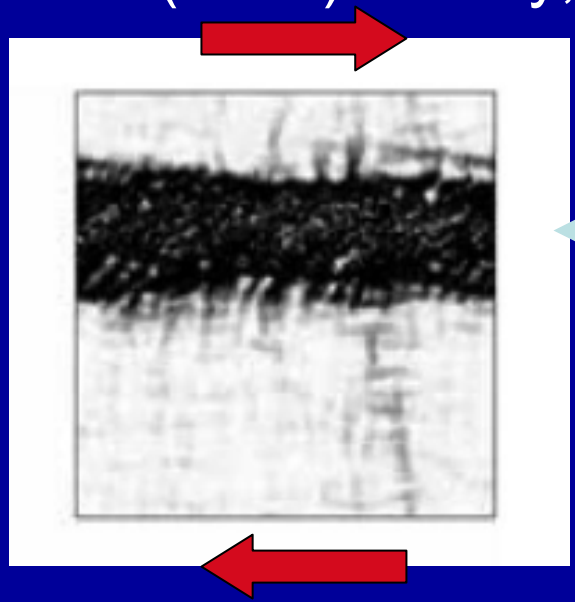
Shear Banding



What causes shear-banding instabilities?

Conventional explanation: Deformation generates heat, which softens the material. But ordinary temperature diffuses too quickly. The effective disorder temperature solves this problem.

Molecular dynamics simulations by Shi, Katz, Li, and Falk, PRL 98, 185505 (2007): Binary, 2-D alloy in simple shear.



Position y

Shear band (darker means greater strain)

STZ theory by Lisa Manning, JSL, and J. Carlson, PRE, 76, 056106 2007

Shi-Falk Analysis

Position (y) dependent strain rate and effective temperature:

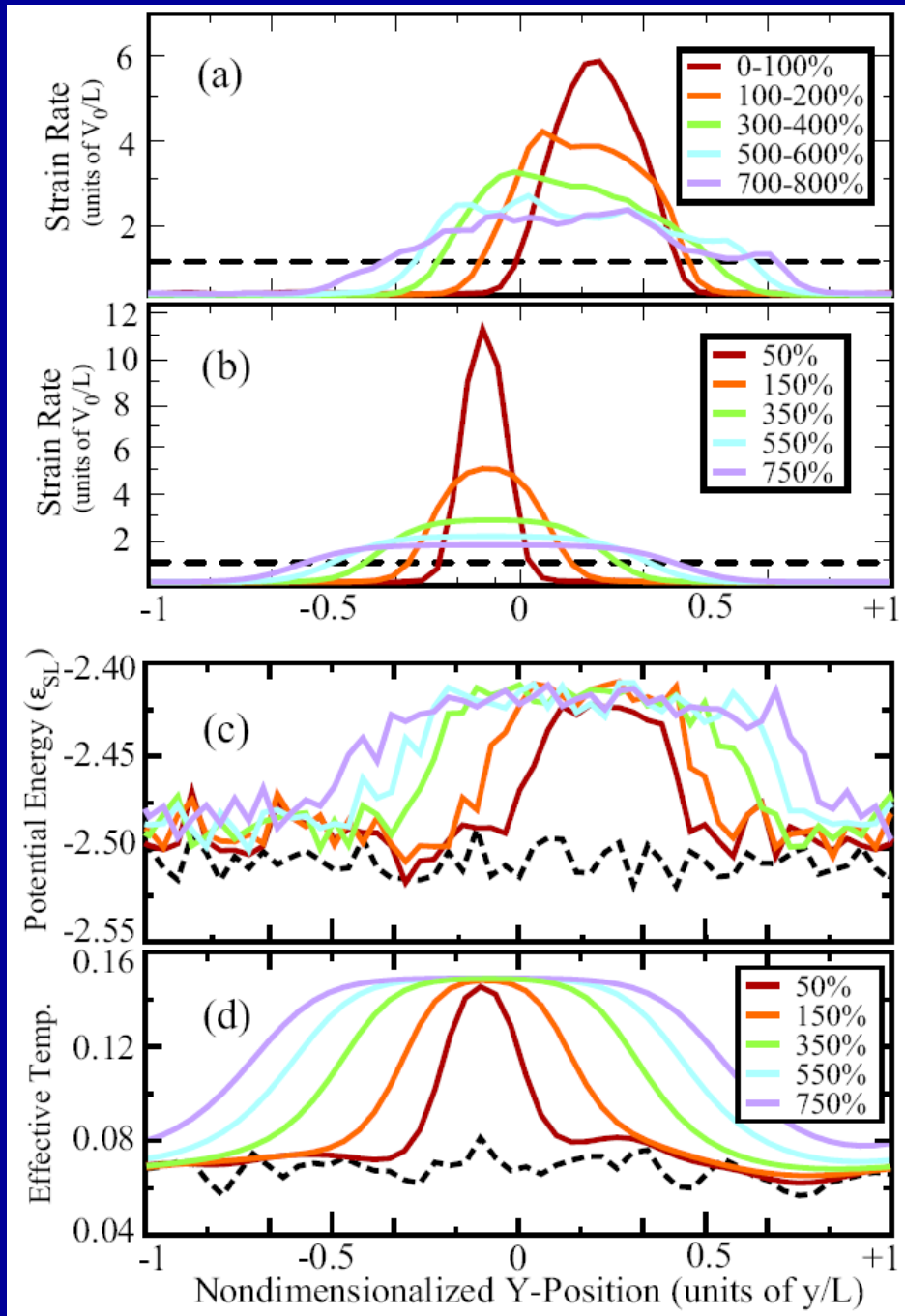
$$\dot{\varepsilon}^{pl}(y) = exp\left(-\frac{e_Z}{\chi(y)}\right)\Psi(\sigma,\theta)$$

The stress σ is constant across the system. Therefore, this relation gives values of ℳ(y,t) up to constants. Then make the quasi-thermodynamic assumption that the potential energy per atom is

$$U(y) \sim constant + C\,\mathcal{M}(y)$$

which gives another measure of ℳ(y,t) up to constants.

The two estimates of ℳ(y,t) agree in detail for several different quenching histories.



Comparison between theory and simulations

The Y axis is the position across the width of the strip.

Note that the band spreads over very long times, i.e. strains 100% - 800%.

Hypothesis: potential energy proportional to ♍.

Bottom panels: comparison between observed potential energy and theoretical effective temperature ♍.

Nonlinear instability: A large enough local increase in ♍ causes the stress to drop everywhere, thus localizing the strain rate.

A question for this KITP program: What are the relations between STZ and SGR? They seem to be trying to solve closely related problems.

An example: Stress relaxation after a strain step:

$$\dot{\sigma} \sim -e^{-1/\chi}\sigma$$

Aging: $\dot{\chi} \sim -e^{-\beta/\chi}\chi$ (Lemaitre's equations)

These equations seem to reproduce some (all?) of the SGR results. JSL thinks that this *might* be a simpler and more physical rheological theory.