Two-level systems in ultrastable glasses

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SIMONS FOUNDATION




with Dmytro Khomenko, Camille Scalliet, Ludovic Berthier, Dave Reichman

`D.Khomenko, C.Scalliet, L.Berthier, D.Reichman, FZ, Phys.Rev.Lett. (2020)`

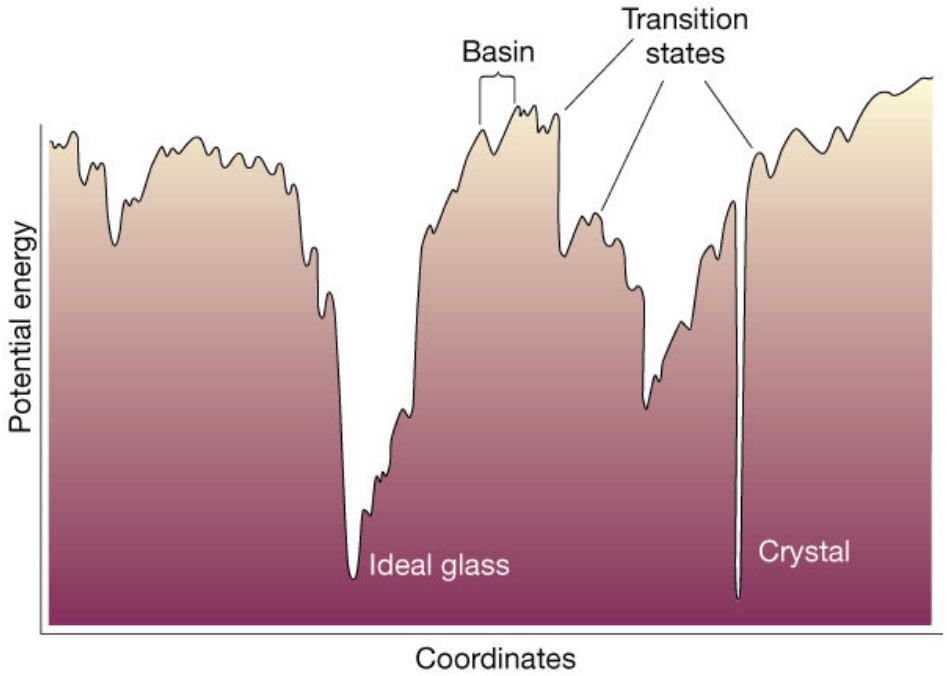
`D.Khomenko, D.Reichman, FZ, Phys.Rev.Materials (2021)`

+ work in progress with Felix Mocanu and Simone Ciarella


Outline

Potential energy landscape (PEL)

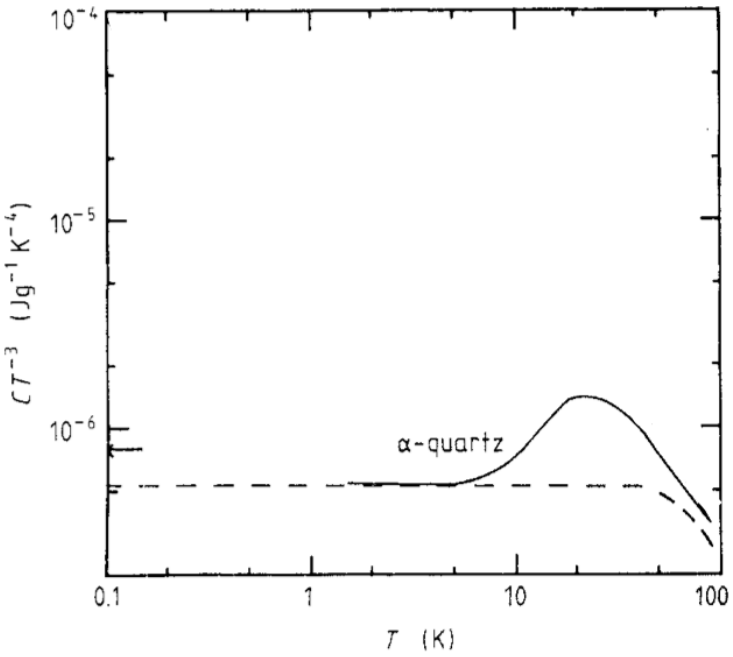
Atomic system with Hamiltonian $H = \sum_i \frac{p_i^2}{2m} + V(\{x_i\})$



Established view of a crystal within the PEL:

- equilibrium *(or very long-lived metastable)* state of matter
- crystal properties are independent of the preparation protocol
- highly symmetric minimum of potential energy (the lattice)
- small harmonic vibrations at low temperature (the phonons)

Crystal - specific heat and thermal conductivity



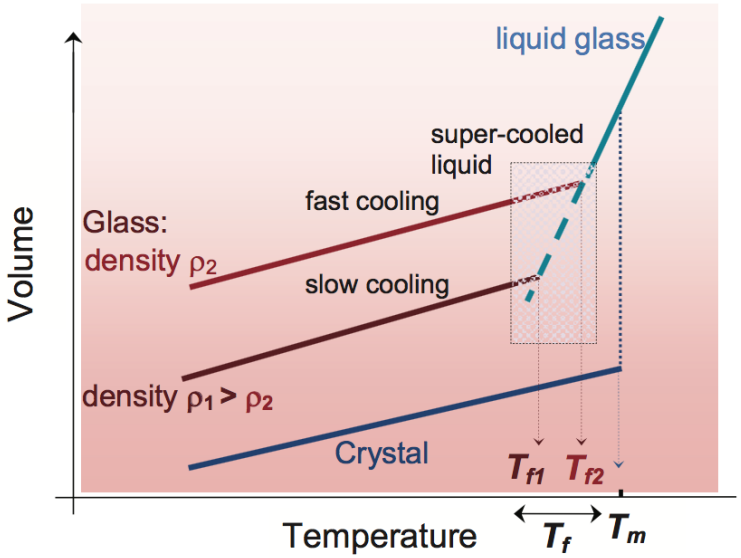
Vibrational density of states: $D(\omega) \sim \omega^2$

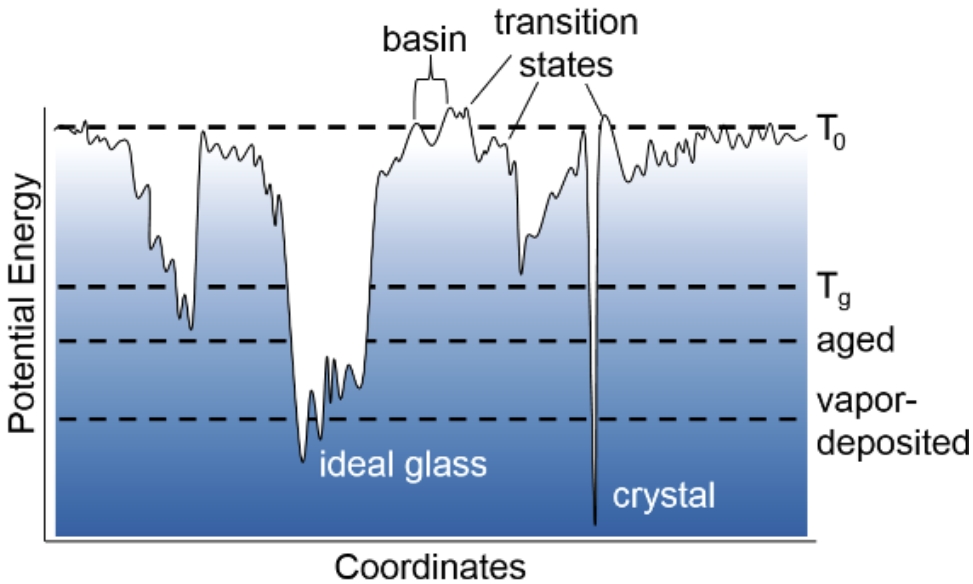
Specific heat $C = \int d\omega D(\omega) c(\beta\hbar\omega/2) \sim T^3$, $\quad c(u) = \frac{u^2}{\sinh(u)^2}$

Thermal conductivity $\kappa = \int d\omega D(\omega)\alpha(\omega)c(\beta\hbar\omega/2) \sim T^3$, $\quad \alpha(\omega) = \frac{c\ell(\omega)}{3} \sim cL_{\text{sample}}$ at low ω

Glass - preparation protocol and fictive temperature

Glass is a *non-equilibrium* state of matter. Its properties depend on the preparation protocol.





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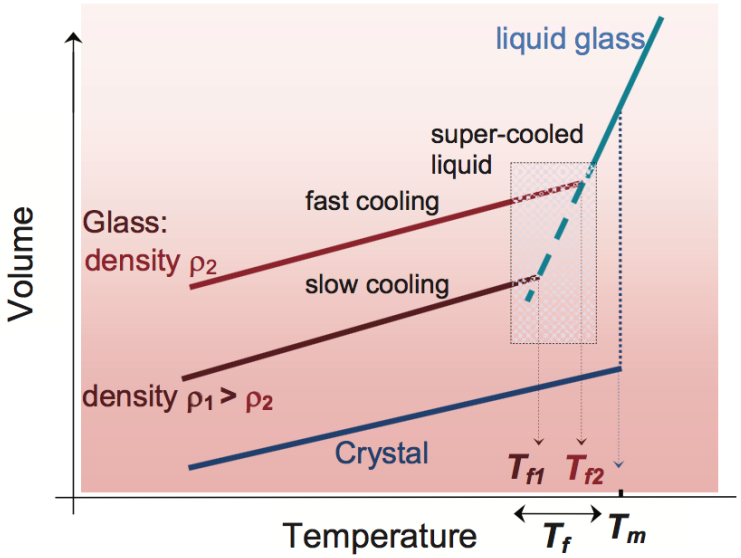
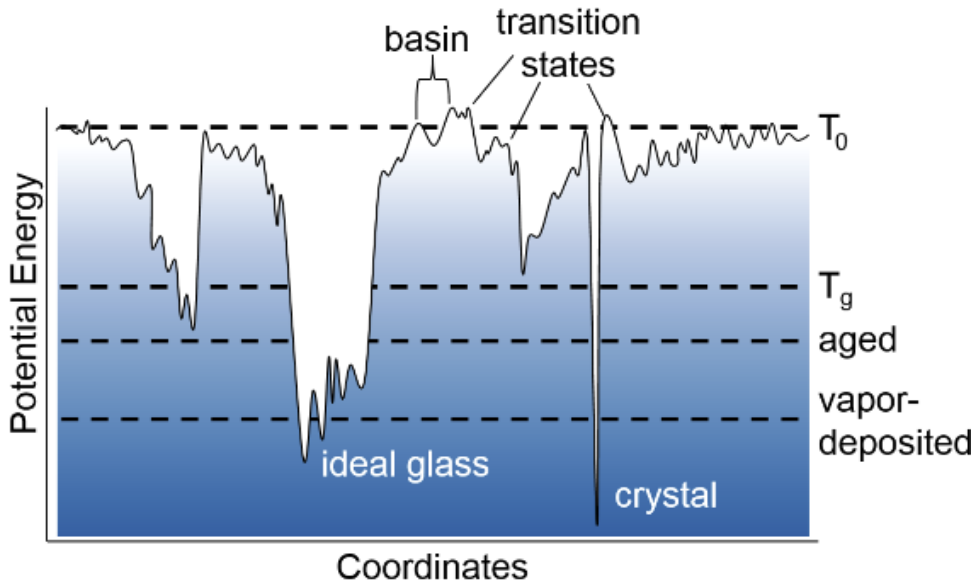


Tool's *fictive temperature* T_f is the temperature at which the glass would find itself in equilibrium if suddenly brought to it from its given state

Hypothesis: T and T_f control all glass properties
Glass = liquid at T_f, then arrested



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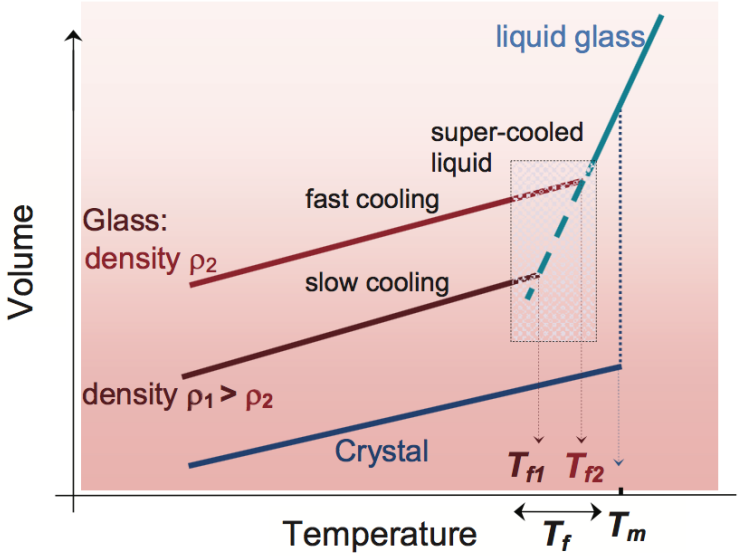

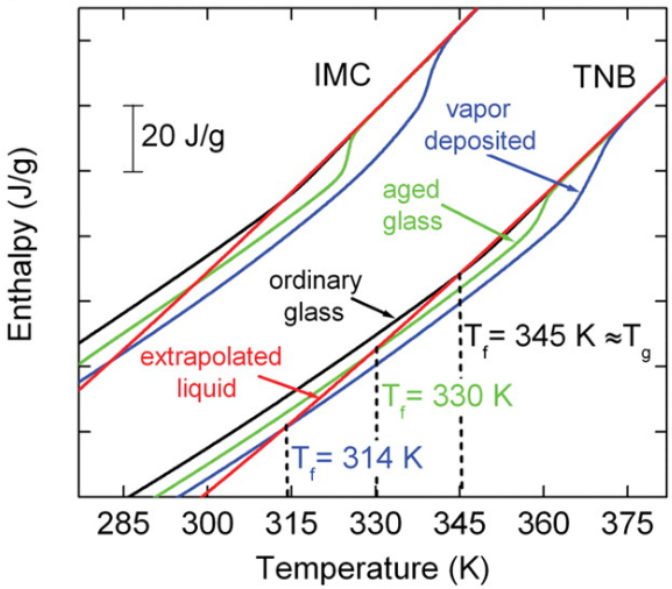

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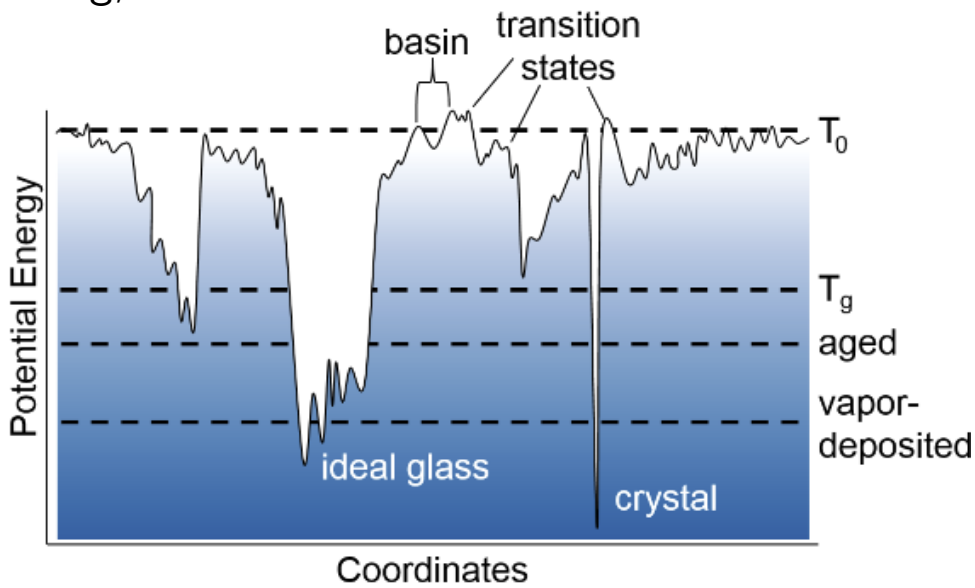
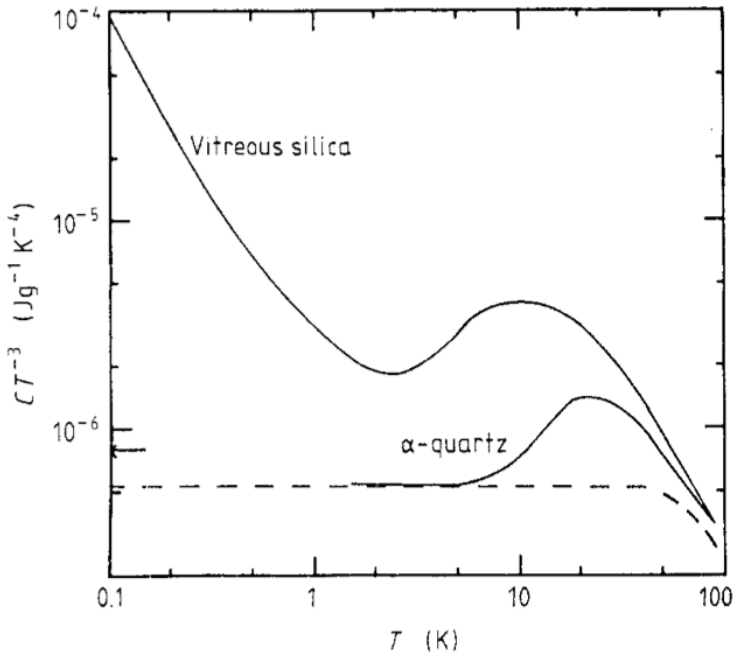
Glass = liquid at T_f, then arrested

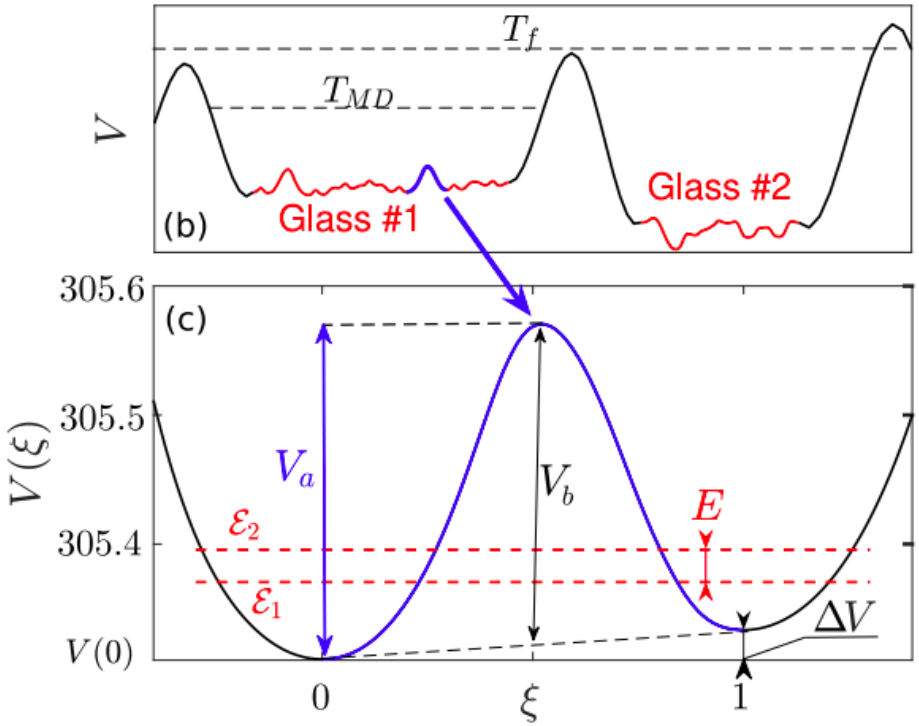
Liquid relaxation time $\tau_\alpha(T_f)$ measures glass stability
By definition $\tau_\alpha(T_g) = 100s$

Glasses with lower T_f are more stable towards heating, shearing, ...



Glass - specific heat





Experimental observation: $C \sim T$

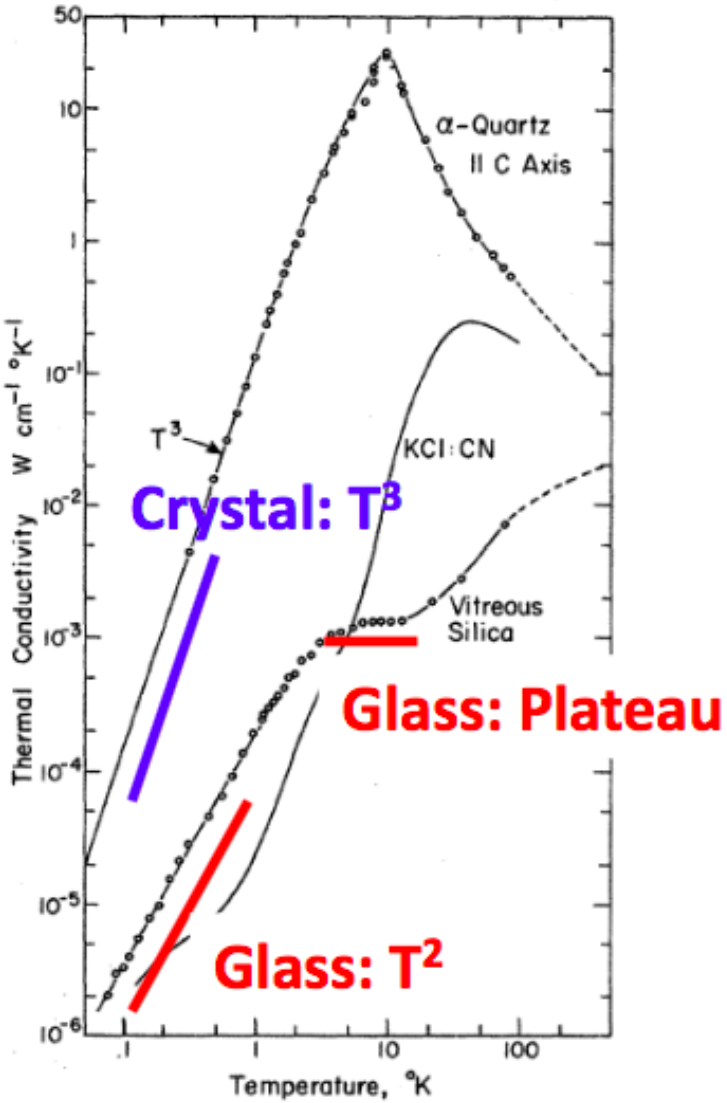
Theory postulates the existence of *tunnelling two-level systems* (TLS) within the glass

$$H = \frac{1}{2}\begin{pmatrix} \Delta & \Delta_0 \\ \Delta_0 & -\Delta \end{pmatrix} \quad \Rightarrow \quad E = \sqrt{\Delta^2 + \Delta_0^2}$$

Specific heat $C \sim \int dE\, n(E)\mathcal{C}(\beta E/2)$, $\quad \mathcal{C}(u) = u^2/\cosh(u)^2$

If $n(E) \sim n_0$ for $E \to 0$, then $C \sim T$ Defects with arbitrarily small activation energy!

Glass - thermal conductivity



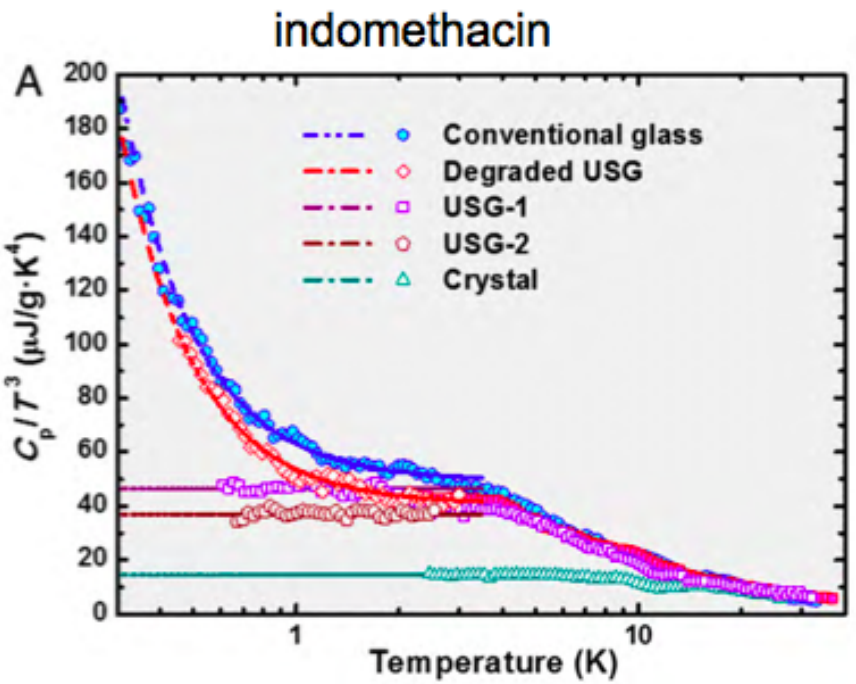
Experimental observation: $\kappa \sim T^2$

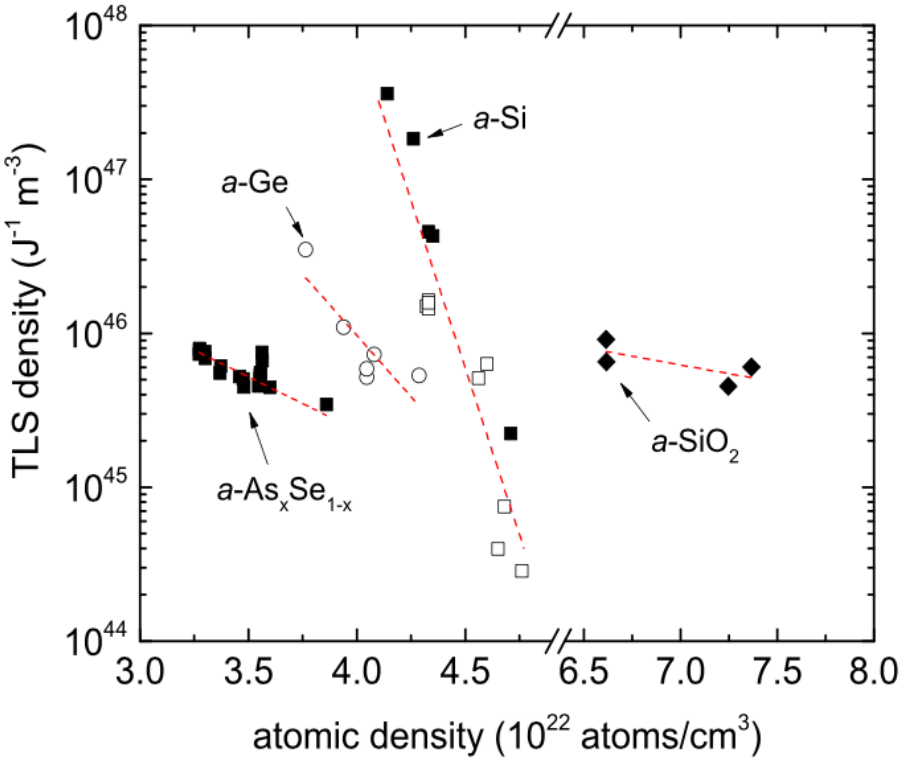
$$\kappa = \int d\omega D(\omega)\alpha(\omega)c(\beta\hbar\omega/2) \quad \Rightarrow \quad \alpha(\omega) \sim \ell(\omega) \sim \omega^{-1}$$

Different from naive expectation of Rayleigh scattering in disordered systems $\ell(\omega) \sim \omega^{-4} \quad \Rightarrow \quad \kappa \sim 1/T$ (perhaps observed at higher temperatures)

Consistent with TLS theory: resonant scattering of phonons on TLS predicts $\ell(\omega) \sim \omega^{-1}$

Glass - dependence on fictive temperature





The density of TLS depends strikingly on glass stability, i.e. on T_f

Note: remarkable universality of TLS density across many different materials

Open questions

TLS theory postulates the existence of "defects" with arbitrarily small excitation energy

- Origin of universality?
- Does T_f control the density of defects?
- Real-space nature of defects: localized or extended?
- Organization of defects in the PEL: random or structured?
- Relation between defects and excitations (vibrational modes)
- Can we see these defects in a numerical simulation?

Outline

A simple model glass

N particles in a volume $\mathcal{V}$, thermodynamic limit, $\rho = N/\mathcal{V}$

Hamiltonian $H = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} v\left(\frac{|x_i - x_j|}{\sigma_{ij}}\right)$ (classical or quantum)

Soft spheres interaction potential $v(r) = \epsilon \frac{1}{r^{12}}$

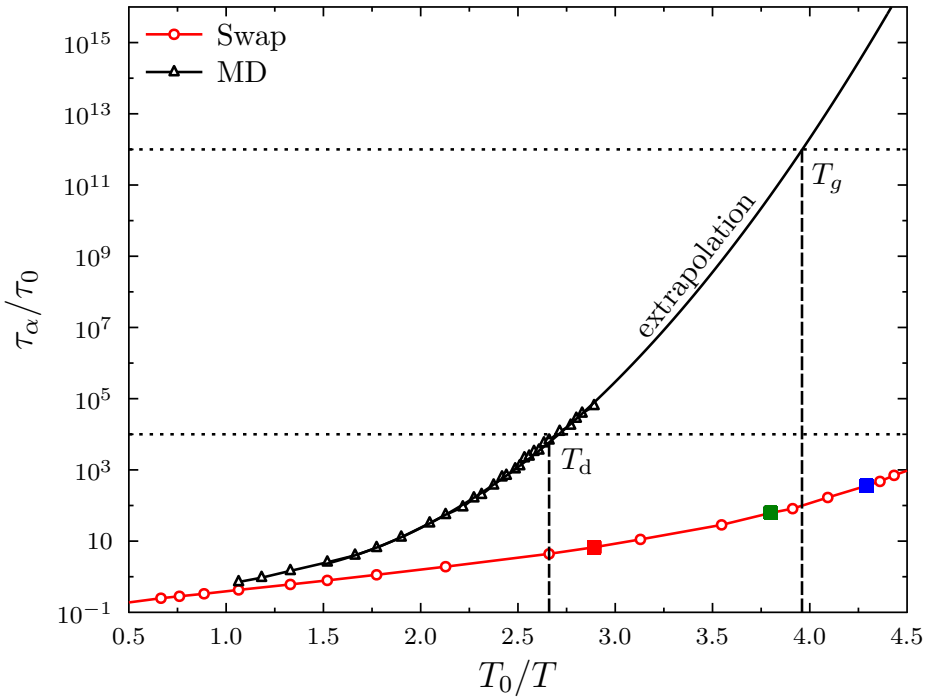
Polydisperse mixture $P(\sigma_m \leq \sigma \leq \sigma_M) \sim 1/\sigma^3$, with $\sigma_m/\sigma_M = 0.45$, polydispersity 23%
Non-additive mixture $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)(1 - 0.2|\sigma_i - \sigma_j|)$

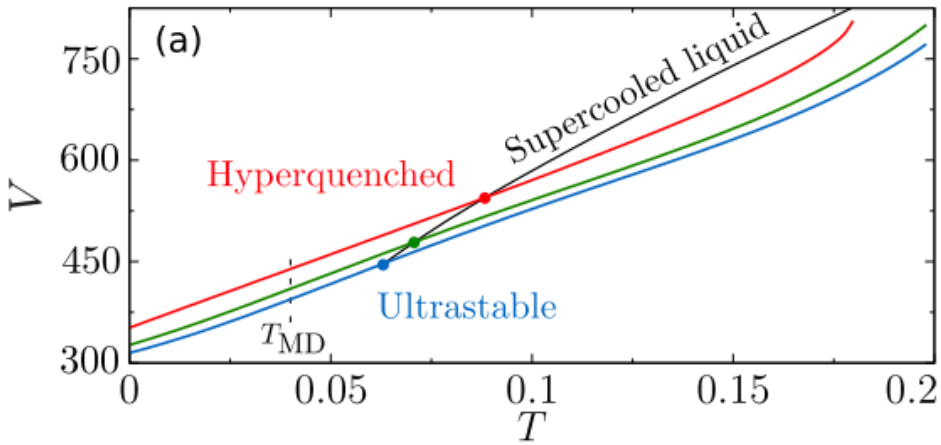
Units $\epsilon = 1$, $m = 1$, $\langle\sigma\rangle = 1$ and $\rho = 1$

The swap algorithm

Unphysical dynamics, designed to speed up equilibration with respect to physical dynamics

$\varphi = 1,\ T_0 = 0.266,\ \tau_\alpha(T_0) = 10^3$ $\qquad$ $T_\mathrm{d} \sim 0.1,\ T_g \sim 0.067$



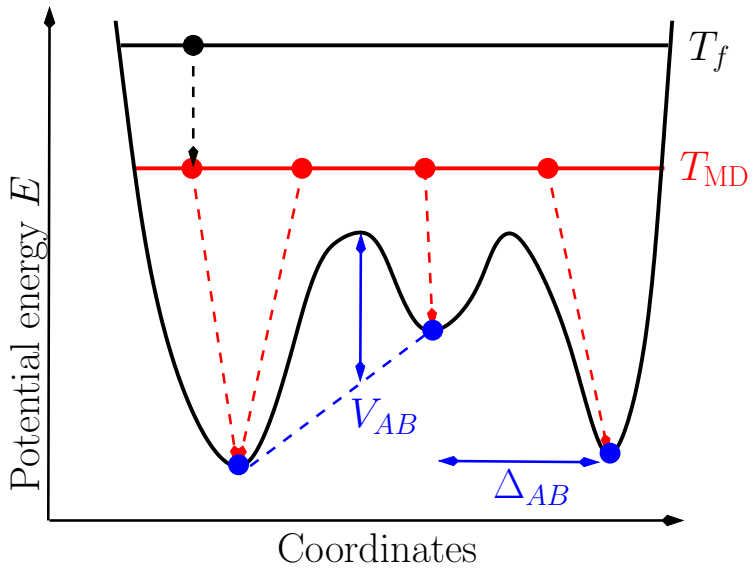


Tune T_f/T_g to explore a wide range of stability, from hyperquenched to ultrastable

Landscape exploration

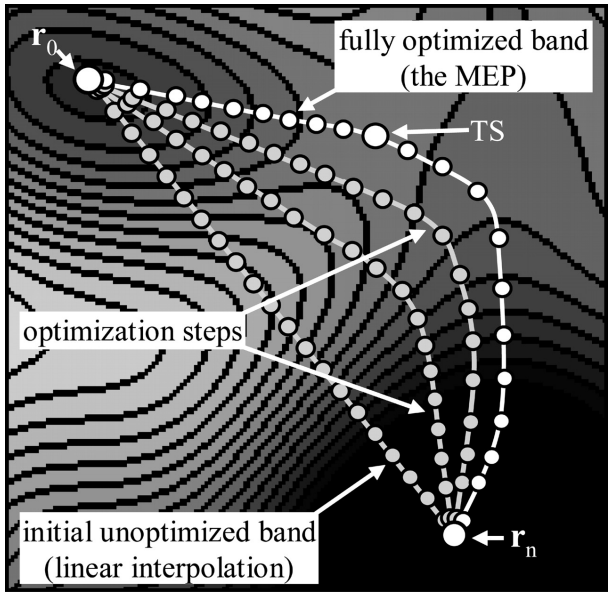
Protocol to explore the PEL *within a given glass*:

- Start from one equilibrium configuration at temperature T_f
- Run MD at $T_{\mathrm{MD}} < T_f \Rightarrow$ produce 'clones'
- Quench clones to nearest energy minimum or 'inherent structure'

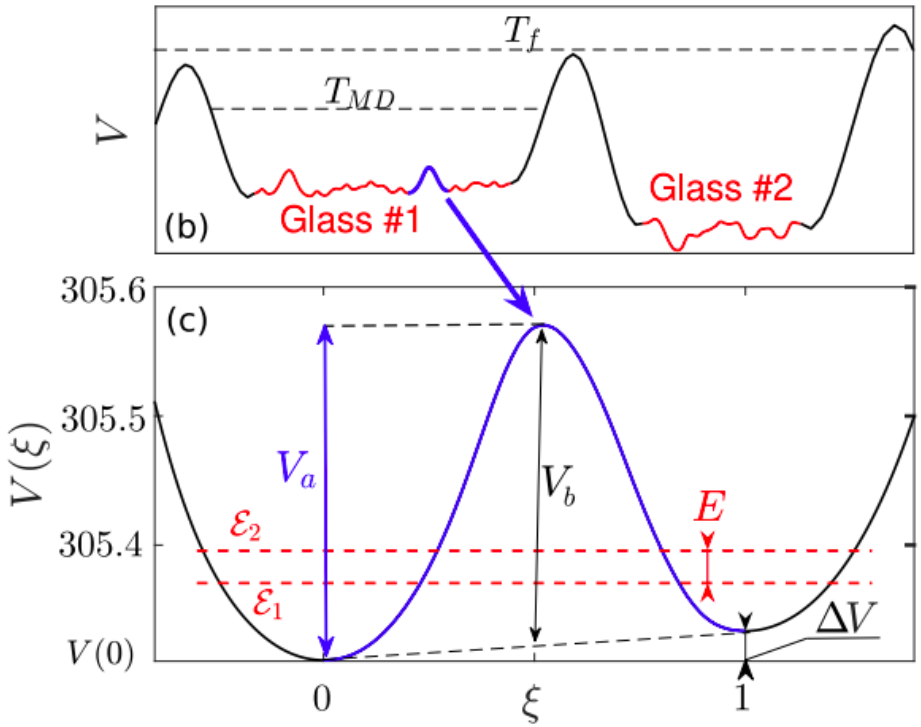


Pair A, B in the library of minima, $\delta r^i_{AB} = r^i_A - r^i_B$:

- Distance $\Delta_{AB} = \frac{1}{N}\sum_i |r^A_i - r^B_i|^2$
- Participation ratio $P_{AB} = \dfrac{\left(\sum_{\mu,i}(\delta r^{\mu,i}_{AB})^2\right)^2}{\sum_{\mu,i}(\delta r^{\mu,i}_{AB})^4}$
- Barrier V_{AB} via Nudged Elastic Band method (only for a well chosen subset of pairs)



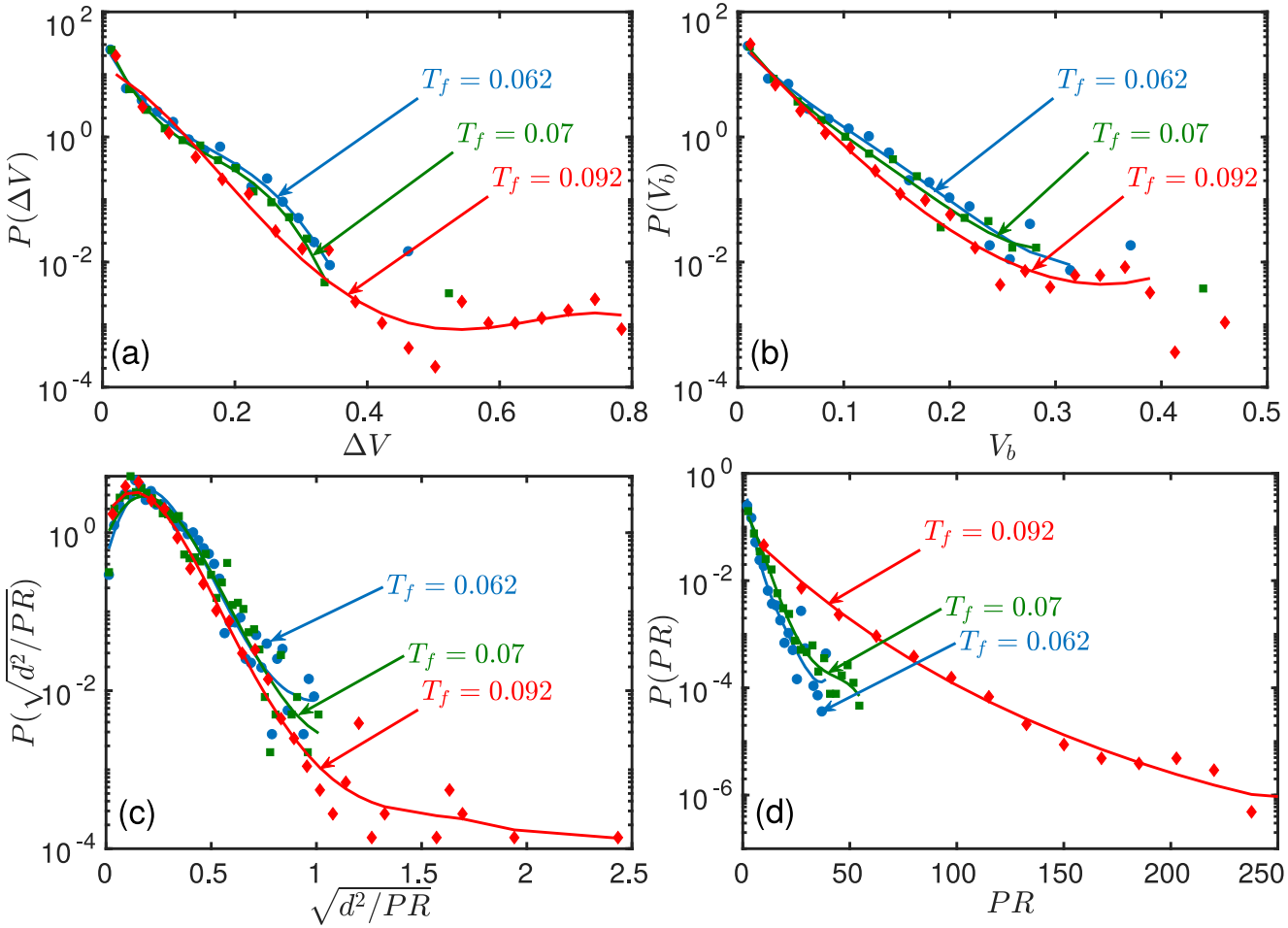
From classical to quantum



- Library of classical double well potentials
- Assumption: quantum effects are only relevant for tunnelling at very low T, *not for landscape exploration*.
- Solve 1D Schrödinger equation along the reaction coordinate of each double well potential. *Extrapolation of $V(\xi)$ on both sides.*
- Many-body nature partially taken into account by integrating transverse directions. *Very rough approximation!*

Outline

Result 1: stability dependence

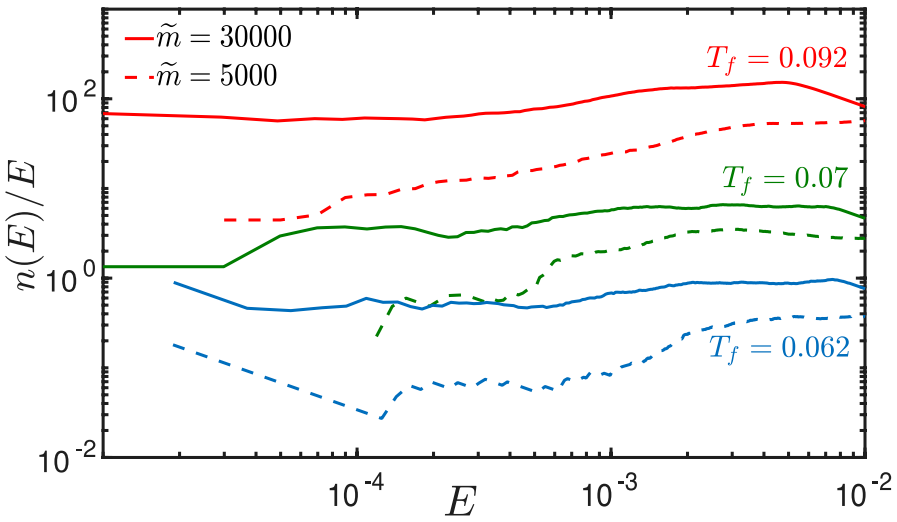


Exhaustive sampling of the PEL:

$T_f = 0.092$	hyperquenched	15 samples	56600 minima/sample	$\langle PR \rangle = 12$
$T_f = 0.07$	conventional	50 samples	540 minima/sample	$\langle PR \rangle = 5.3$
$T_f = 0.062$	ultrastable	200 samples	66 minima/sample	$\langle PR \rangle = 4.1$

Result 2: quantum effects

Solve 1D Schrödinger equation in each double well potential $\Rightarrow$ quantum splitting E
Dimensionless mass $\widetilde{m} = m\sigma^2\varepsilon/\hbar^2$



- Two-orders of magnitude reduction of n_0 with T_f: consistent with experiments
- Good statistics in the relevant range of E: direct observation of TLS

$$H = \frac{1}{2}\begin{pmatrix} \Delta & \Delta_0 \\ \Delta_0 & -\Delta \end{pmatrix} \quad \Rightarrow \quad E = \sqrt{\Delta^2 + \Delta_0^2}$$

$$n_c(E) = \{\text{nb. of TLS with splitting} < E \text{ per atom and per sample}\} \sim n_0 E$$

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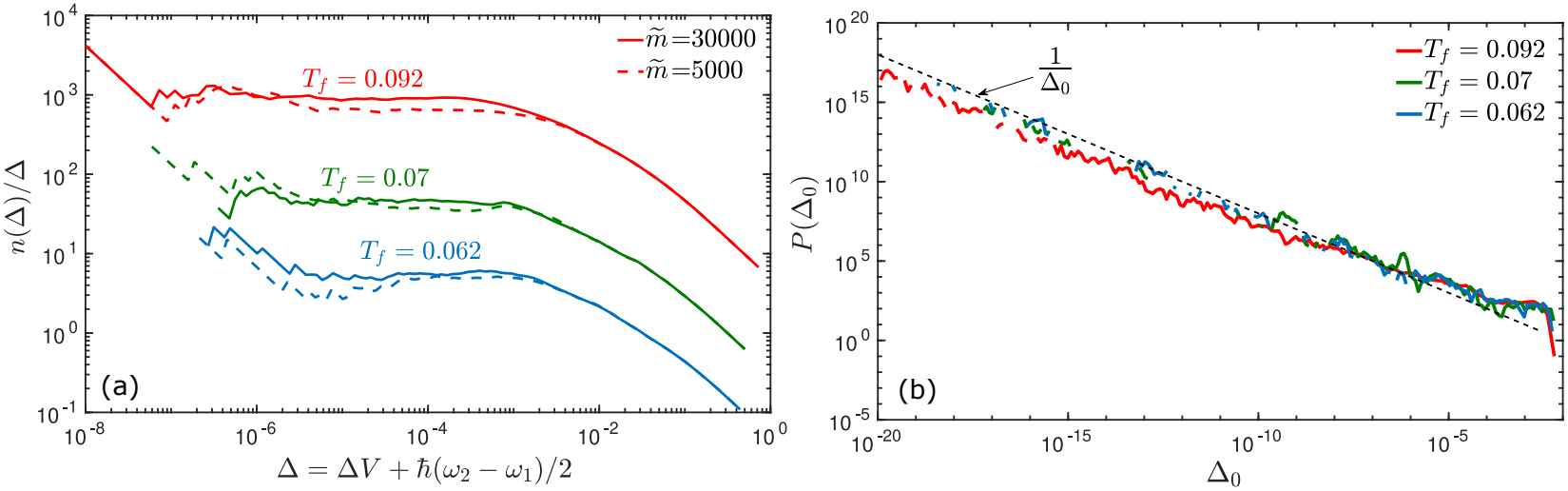

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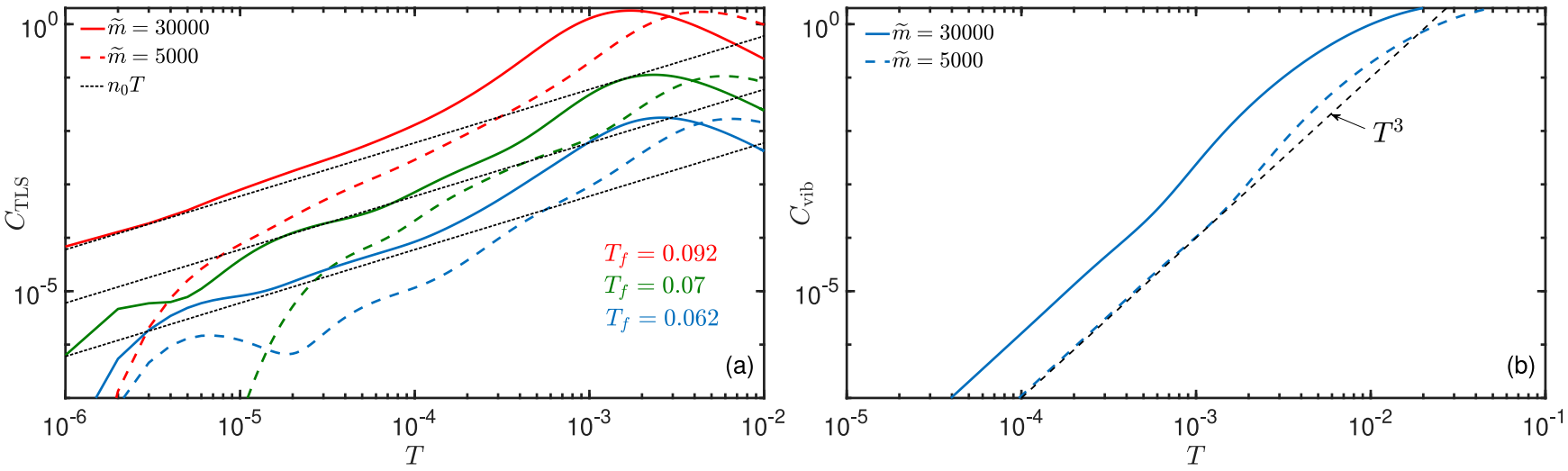

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- Good statistics in the relevant range of E: direct observation of TLS
- Specific heat of TLS dominant over vibrational contribution

$$C_{\rm TLS} \sim \int dE\, n(E)\mathcal{C}(\beta E/2) \sim T\ , \qquad \mathcal{C}(u) = u^2/\cosh(u)^2$$
$$C_{\rm vib} = \int d\omega D(\omega) c(\beta\hbar\omega/2) \sim T^3\ , \qquad c(u) = \frac{u^2}{\sinh(u)^2}$$

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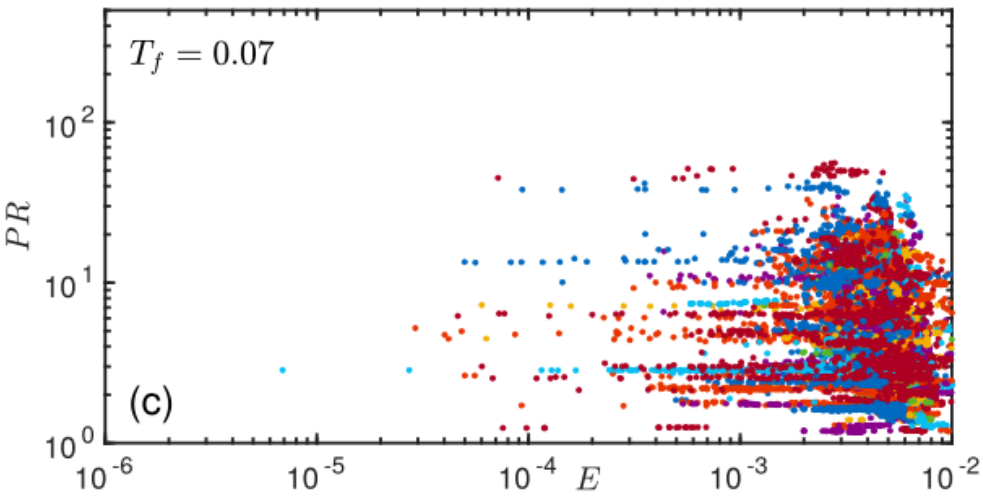

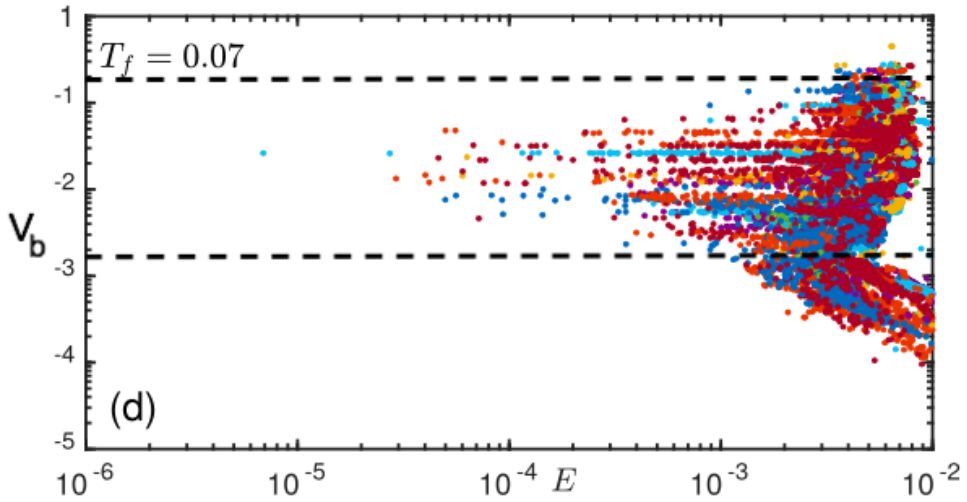

- Two-orders of magnitude reduction of n_0 with T_f: consistent with experiments
- Good statistics in the relevant range of E: direct observation of TLS
- Specific heat of TLS dominant over vibrational contribution
- TLS are mostly localized but occasionally can have $PR \sim 200$
- We observe that $10 < \frac{V_b}{k_B T_Q} < 1000$ as predicted by Anderson-Halperin-Varma

Result 2: quantum effects

Solve 1D Schrödinger equation in each double well potential $\Rightarrow$ quantum splitting E
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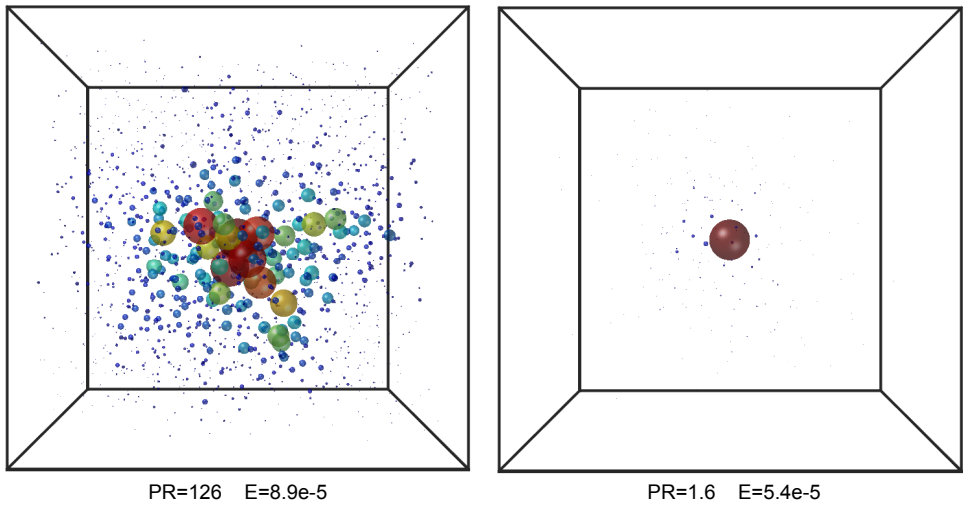

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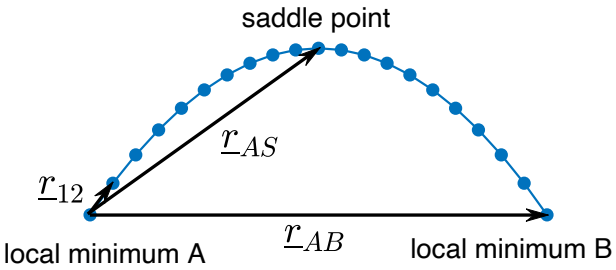
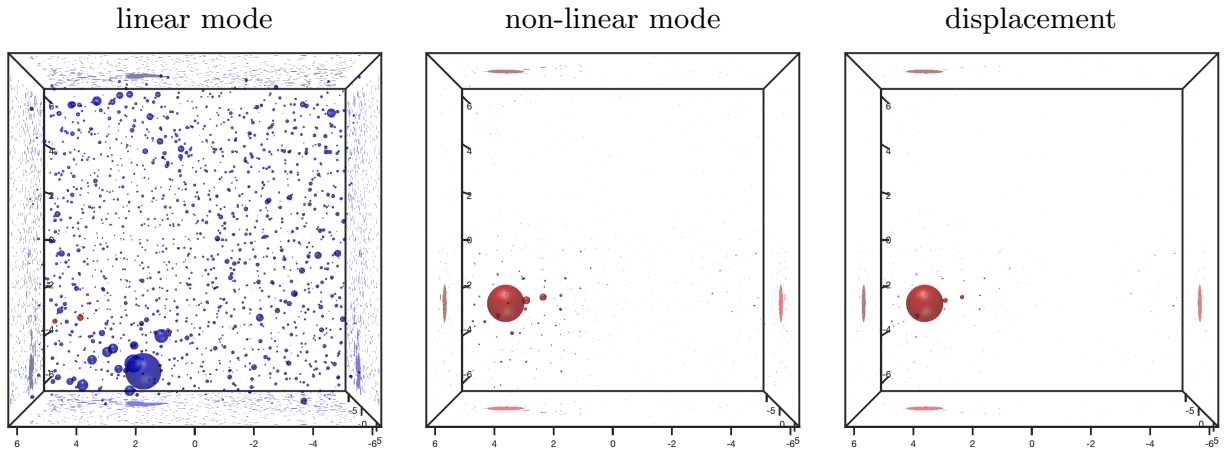
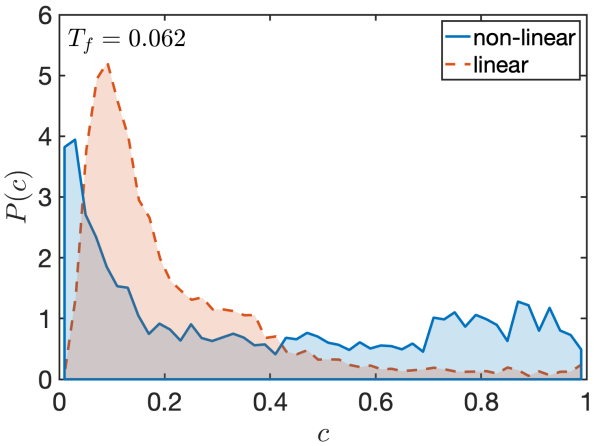
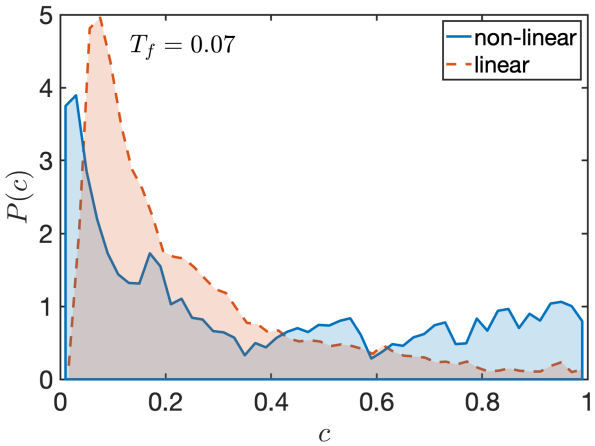
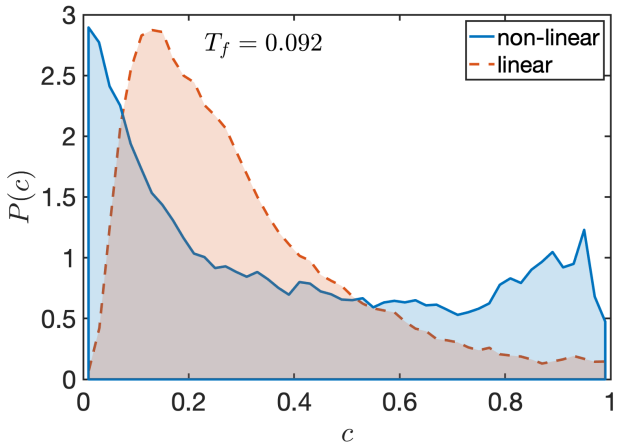
Result 3: TLS and soft spots





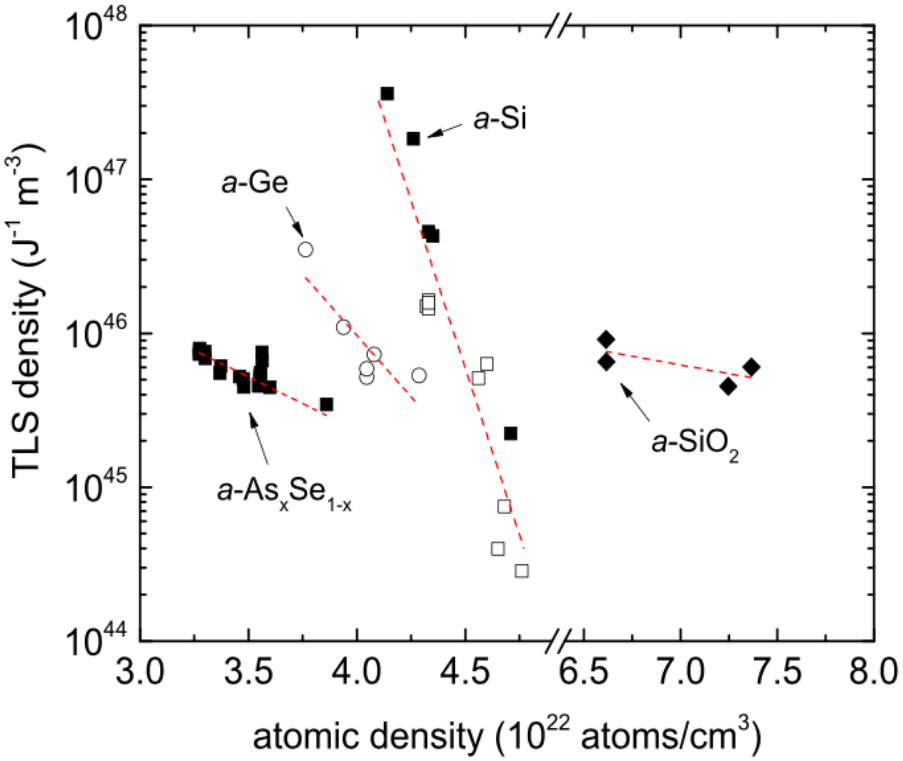






- Tangent vector $\underline{r}_{12}$ is parallel to a soft mode $\Rightarrow$ soft spots close to TLS in real space
- The overlap $c = |\hat{r}_{AB} \cdot \hat{r}_{\mathrm{mode}}|$ is small $\Rightarrow$ different displacement fields

Puzzle: counting TLS in the PEL



- For our systems at $T_f = 0.092, 0.07, 0.062$ we get $n_0 \sim 10^{50}, 10^{49}, 10^{48}$ J^{-1} m^{-3}
- Does polydispersity (or sphericity) enhance the number of TLS?
- Is it a counting problem: TLS per sample or TLS per (relevant) minimum?

Outline

Summary

- Thanks to the swap algorithm we can explore the landscape of the model systematically, tuning T_f/T_g for stability.

- Result 1. The number of defects within a glass increases strongly with T_f, while their properties remain mostly invariant, except for an increase in PR.

- Result 2. Rare defects with very low barriers give rise to TLS.
  Assumptions of the TLS theory confirmed microscopically.
  Reduction of TLS with T_f consistent with recent experiments.
  TLS are mostly localized but occasionally extended.

- Result 3. TLS are spatially related to soft spots of the glass.
  But the displacement field of vibrational modes is not a good predictor of that of TLS.

Outline

Ongoing work

1. Universality? What about other models?
   (non-polydisperse, non-spherical particles, directional bonding...)

PHYSICAL REVIEW LETTERS **125,** 085505 (2020)

Ultrastable Metallic Glasses *In Silico*

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[2]*Laboratoire de Physique Statistique, École Normale Supérieure, CNRS, PSL Research University, Sorbonne Université, 75005 Paris, France*
[3]*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

(Received 28 February 2020; accepted 24 July 2020; published 21 August 2020)

We develop a generic strategy and simple numerical models for multicomponent metallic glasses for which the swap Monte Carlo algorithm can produce highly stable equilibrium configurations equivalent to experimental systems cooled more than 10^7 times slower than in conventional simulations. This paves the way for a deeper understanding of the thermodynamic, dynamic, and mechanical properties of metallic glasses. As first applications, we considerably extend configurational entropy measurements down to the experimental glass temperature, and demonstrate a qualitative change of the mechanical response of metallic glasses of increasing stability toward brittleness.

with Felix Mocanu

Ongoing work

2. Better estimation of quantum effects, via path integral calculations

Path-integral calculation of the tunnel splitting in aqueous ferrous–ferric electron transfer

Massimo Marchi and David Chandler
Department of Chemistry, University of California, Berkeley, California 94720

(Received 26 November 1990; accepted 27 March 1991)

We examine path-integral methods for computing electronic coupling matrix elements relevant to long-ranged electron transfer. Formulas are derived that generalize those already found in the literature. These extensions allow for efficient computation, especially for complex systems where there is either no inherent symmetry, or that symmetry is difficult to ascertain *a priori*. The usefulness of the computational methods based on these formulas is demonstrated by carrying out calculations for the ferrous–ferric exchange.

Tunneling splittings from path-integral molecular dynamics using a Langevin thermostat

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Ring-polymer instanton method for calculating tunneling splittings

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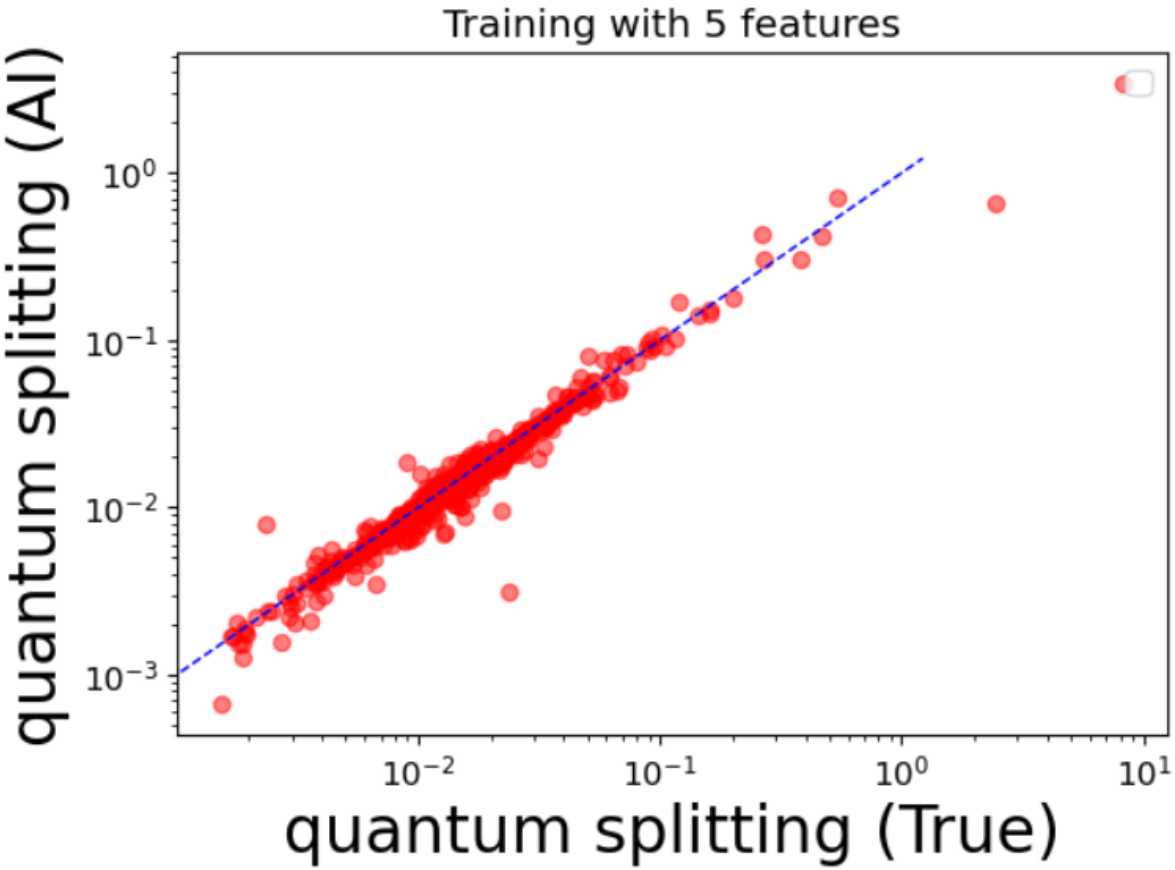
Ongoing work

3. Machine learning to identify TLS without running the NEB
   Input features: pair A, B in the library of minima, displacement field $\delta r^i_{AB} = r^i_A - r^i_B$



with Simone Ciarella




with Dmytro Khomenko, Camille Scalliet, Ludovic Berthier, Dave Reichman

`D.Khomenko, C.Scalliet, L.Berthier, D.Reichman, FZ, Phys.Rev.Lett. (2020)`

`D.Khomenko, D.Reichman, FZ, Phys.Rev.Materials (2021)`

+ work in progress with Felix Mocanu and Simone Ciarella