Comparative Study on the Dynamic Heterogeneity During Critical Gelation

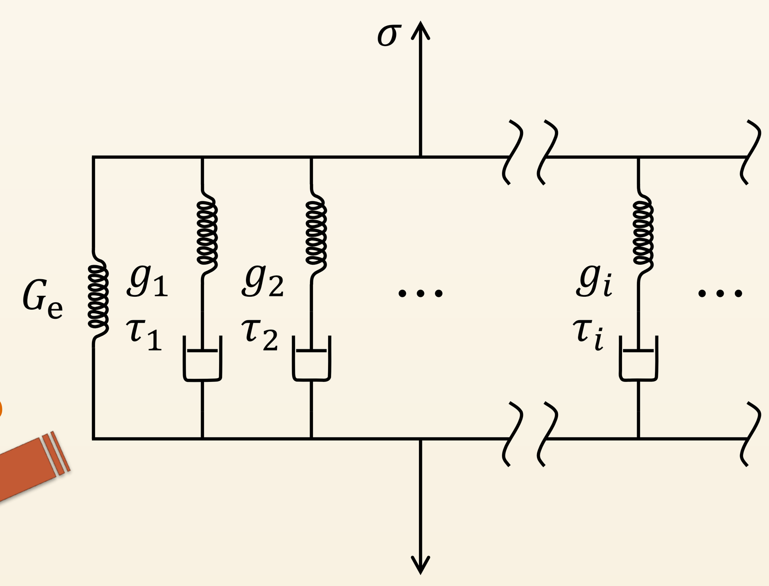
Yingtao Zhang, Yingkang Dai, Xiaogang Ou, Wei Hong, Weixiang Sun*, Zhen Tong

School of Materials Science and Engineering, South China University of Technology

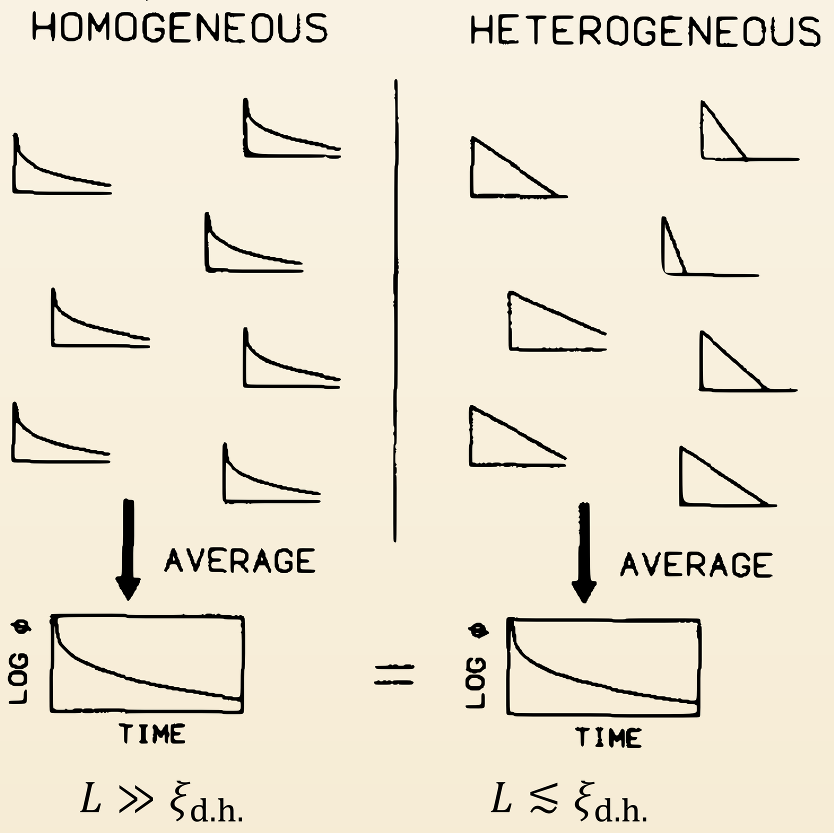
* Corresponding author. Email: mswxsun@scut.edu.cn

Dynamic heterogeneity: spatial fluctuation of relaxation time

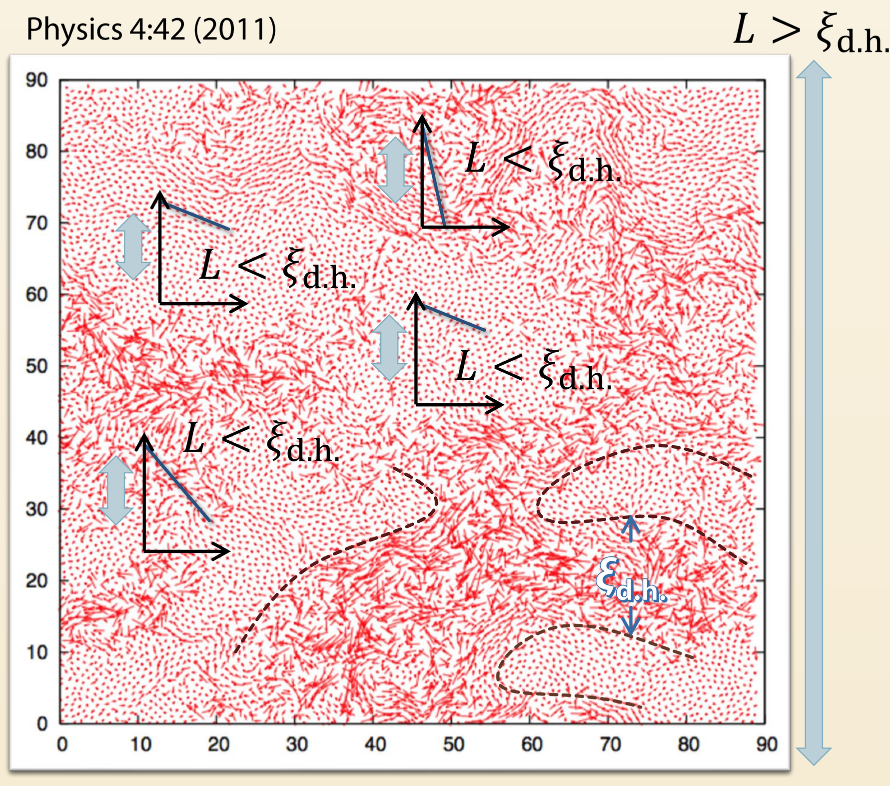
- Complex fluids often exhibit composite spectra of relaxation times, which are understood by the generalized Maxwell model.
- *Are the fast and slow modes only phenomenological? Or are they separately happening somewhere inside the fluids?*



Chem. Phys. Lett. 216:223 (1993)

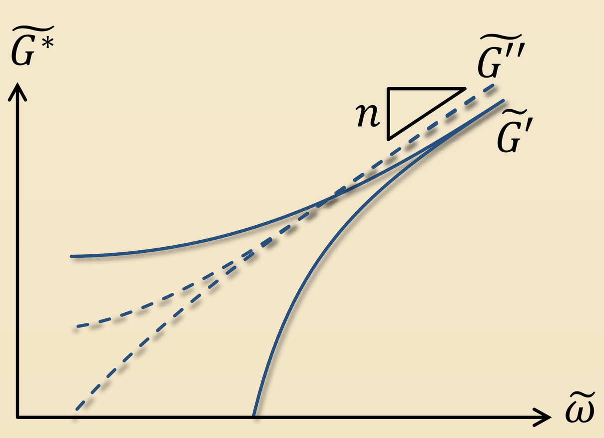


Physics 4:42 (2011)

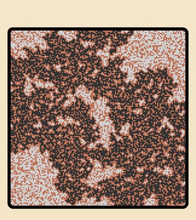


- The answer depends on whether the **observation length scale** L of dynamics is larger than the **characteristic length scale** $\xi_{\mathrm{d.h.}}$ of the system.
- $\xi_{\mathrm{d.h.}}$ is a length above which the dynamic heterogeneity smears out and the system's looks homogeneous with a composite relaxation time spectrum.
- $\xi_{\mathrm{d.h.}}$ is difficult to measure directly by experiment.

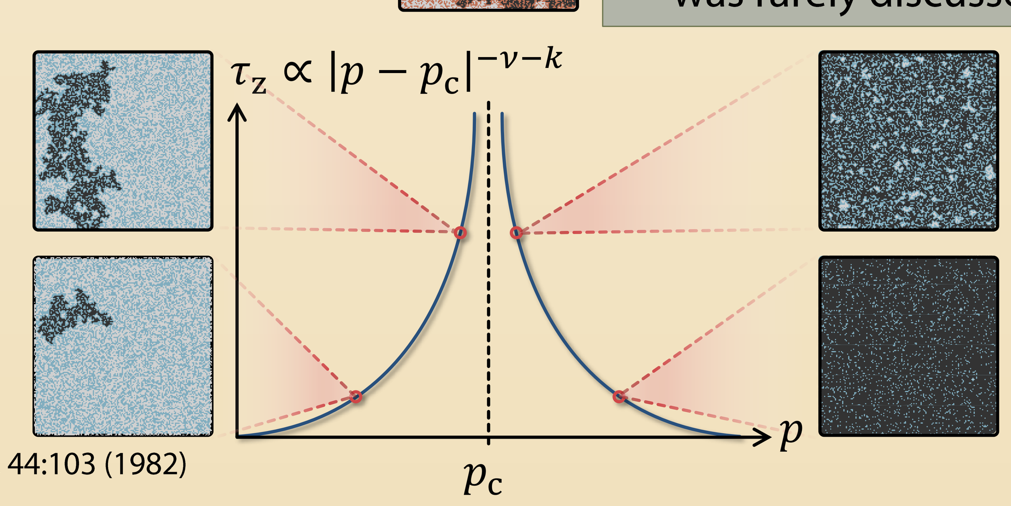
Growing length scale and dynamic criticality during gelation



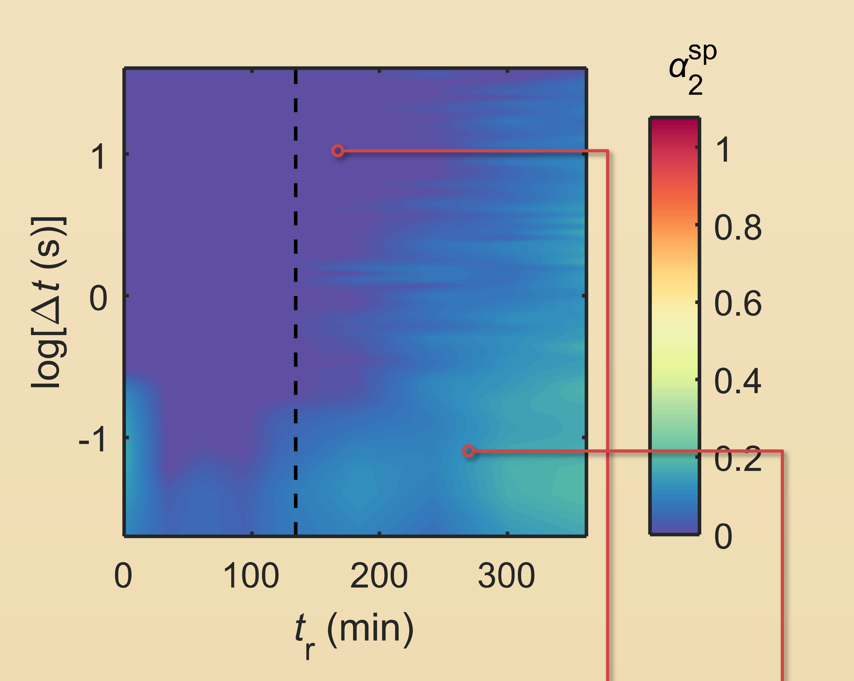
- Gelation is a *dynamic* critical phenomenon.
- Viscoelastic spectrum $G^*(\omega)$ at the critical gel point p_c collapses into master-curves.



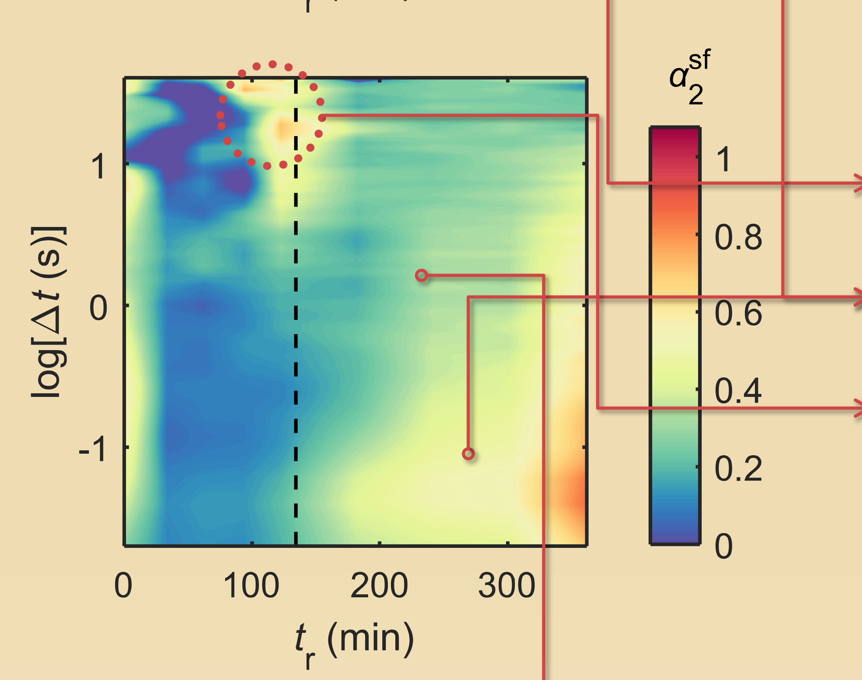
- Average dynamics τ_z diverges critically near p_c, …
- so should $\xi_{\mathrm{d.h.}}$, which however was rarely discussed before.



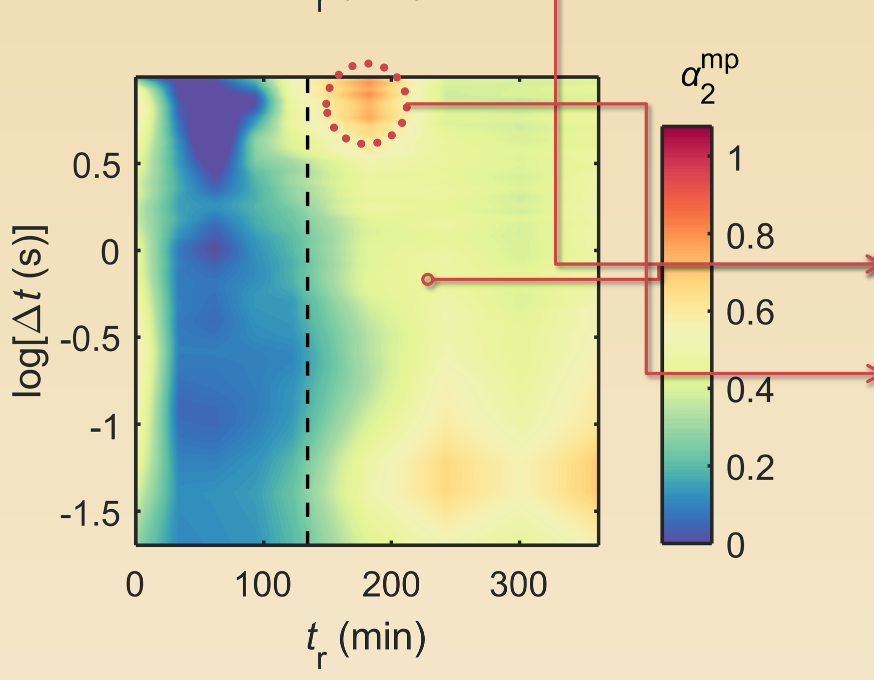
Adv. Polym. Sci. 44:103 (1982)



- **Comparing three non-Gaussian parameters**
  - They differ among each other; extents of heterogeneity are different under different length scales.
  - All show frozen heterogeneity at long reaction times.
  - Initial (t_r = 0) large-scale heterogeneity might be due to sample injection.

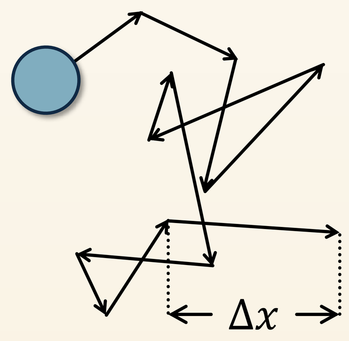


- **Comparing α_2^{sp} vs α_2^{sf}**
  - α_2^{sp} is small; every region of O(1 μm) looks homogeneous, even after gel point.
  - $\alpha_2^{\mathrm{sf}} > \alpha_2^{\mathrm{sp}}$; dynamics differs significantly on O(100 μm).
  - Long-live (**Δ*t*** > 10 s) heterogeneity occurs in α_2^{sf} just before gel point, but not in α_2^{sp}; $\xi_{\mathrm{d.h.}}$ grows over O(100 μm) just before divergence.

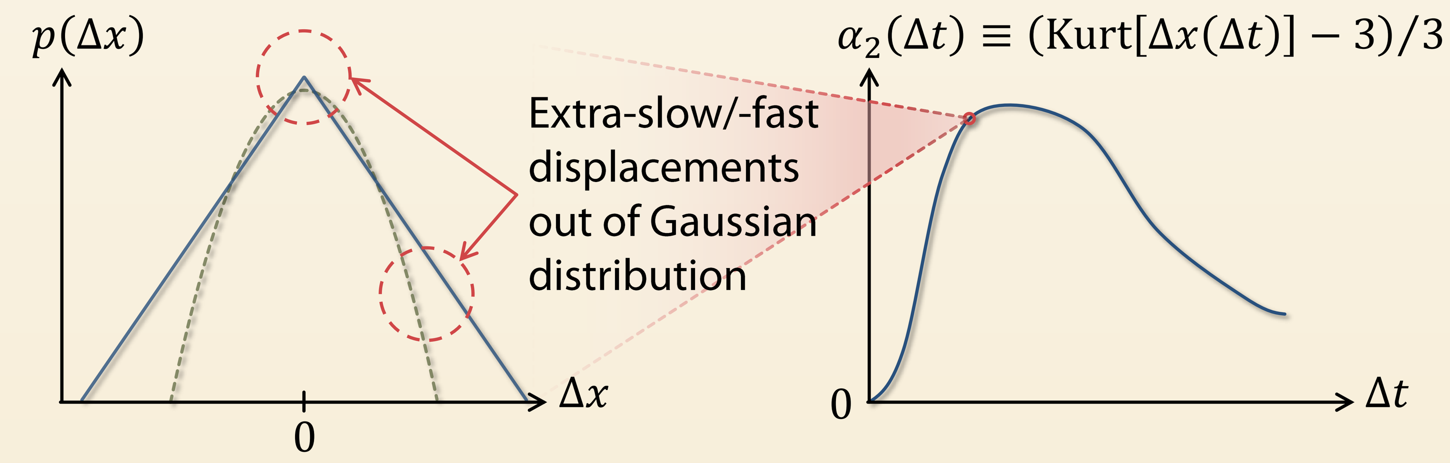


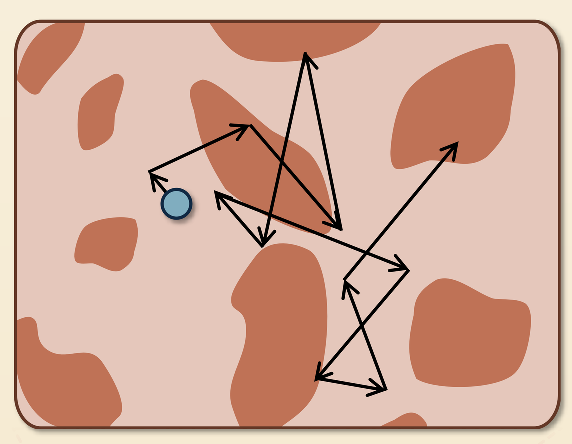
- **Comparing α_2^{sf} and α_2^{mp}**
  - $\alpha_2^{\mathrm{mp}} > \alpha_2^{\mathrm{sf}}$; extra heterogeneity exists on O(1 mm) after gel point!
  - Long-live heterogeneity (red dashed circle) occurs in α_2^{mp} after gel point, where $\xi_{\mathrm{d.h.}}$ decreases below O(1 mm) but not less than O(1 mm), since there is no features at the same place in other two α_2's.

Measuring dynamic heterogeneity by particle tracking microrheology



- The thermal motion of micron-sized particles reflected the *local viscoelasticity* of the fluid medium.
- **Displacements Δ*x*** within a given **lag time Δ*t*** will deviate from Gaussian distribution if the range of the random walk covers regions of slow and fast relaxation.
- The **non-Gaussian parameter α_2**, defined from the kurtosis of the displacements, quantifies *how different the dynamics are* within the range of random walks, but contains *no* information about the length scale $\xi_{\mathrm{d.h.}}$.

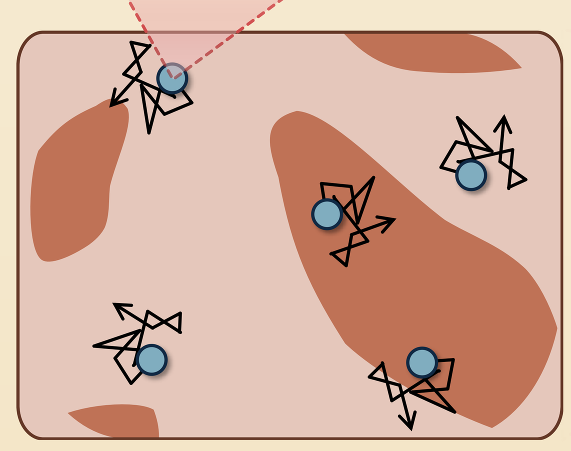


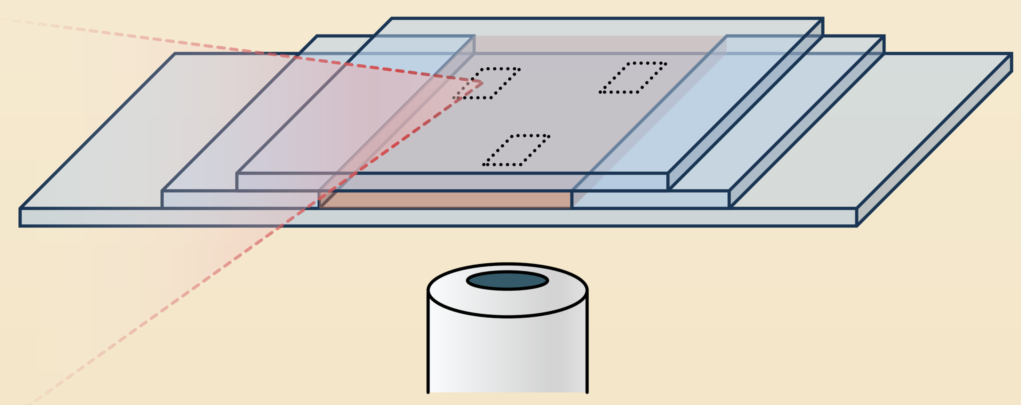


- We varied the observation length scale L by changing the **sample space Ω** of the statistics for α_2.
- α_2 is nonzero when $\xi_{\mathrm{d.h.}}$ and L are of the same order of magnitude.

❶ **Single-particle statistics, α_2^{sp}**
Ω = {all displacements of a single particle}
L ~ region of random walk, O(1 μm)

❷ **Single-FOV statistics, α_2^{sf}**
Ω = {all displacements of all particles in one FOV}
L ~ average distance among adjcent particles, O(100 μm)

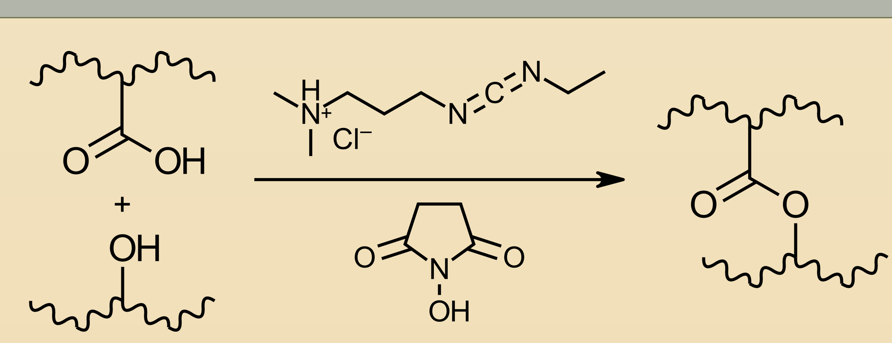




❸ **Multi-FOV statistics, α_2^{mp}**
Ω = {all displacements of all particles in multiple FOVs}
L ~ distance among FOVs, O(1 mm)

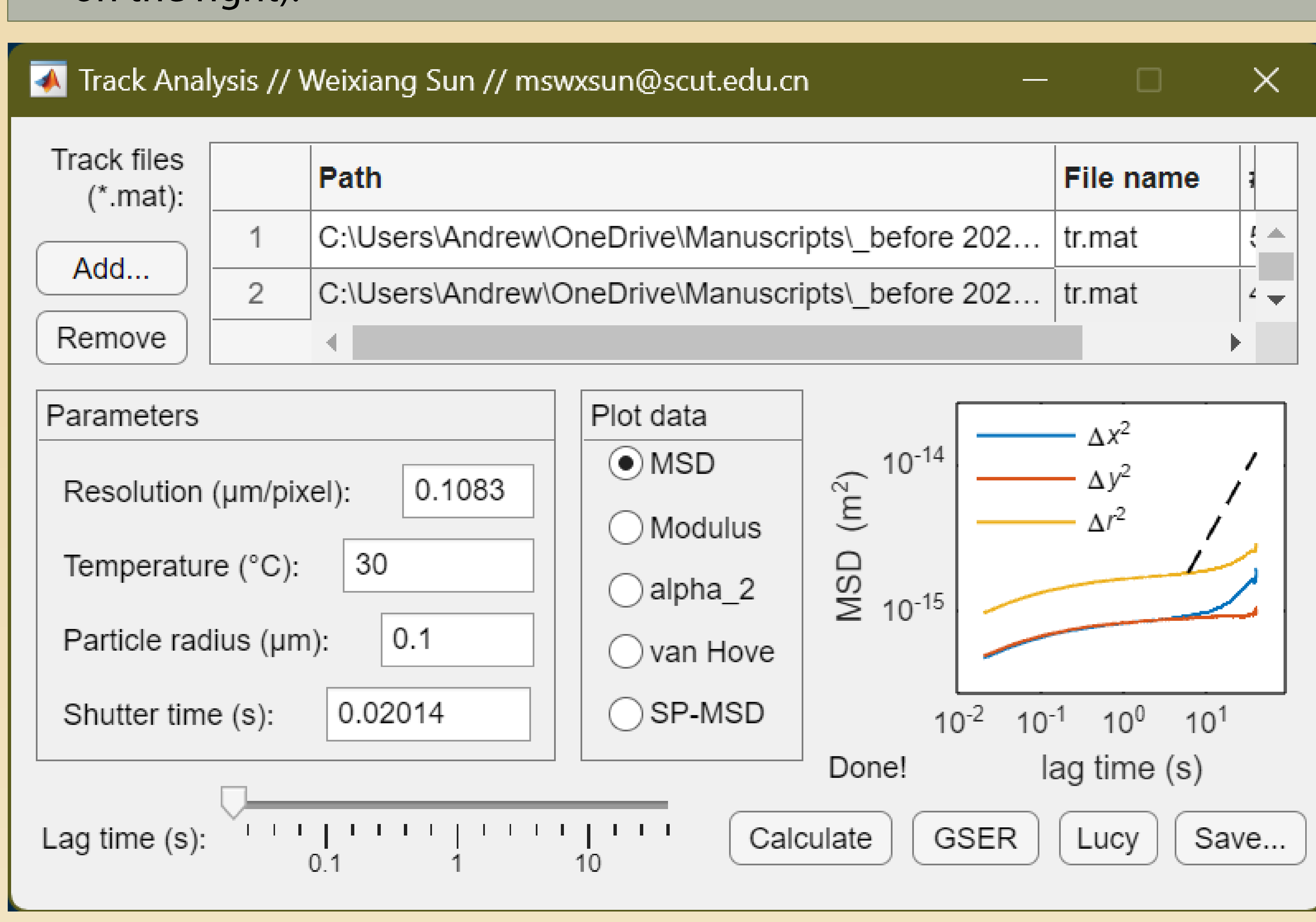
Example: crosslinking of sodium hyaluronate

- We observed the time-dependent crosslinking of sodium hyaluronate *via* inter-chain esterification under the activation by *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS).
- The system reached the critical gel point at **reaction time t_r** = 133 min, determined by the Winter–Chambon criterion.



Conclusions and more

- We proposed a method that enables the detection of growing $\xi_{\mathrm{d.h.}}$ in complex fluids.
- We have successfully tried on more gelling systems, esp. 4-arm PEG gels which are *structurally homogeneous* throughout the gelation (not shown here).
- We have also calculated **4-point susceptibility χ_4** from tracer particles, which provides $\xi_{\mathrm{d.h.}}$ more directly (not shown here).
- We have released a MATLAB app with GUI for multi-FOV track analysis (scan the QR code on the right).



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Acknowledgement

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