On the violation of Stokes-Einstein relation in supercooled water: Role of hydrogen-bond lifetime

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Science Advances 3, e1700399 (2017)

Outline

- Stokes-Einstein relation
  - $D\eta/T$ = const.
- Violation of SE relation in glasses
  - non-Gaussian property?
  - Is there a unified concept?
- Violation of SE relation in supercooled water
  - direct calculation of shear viscosity from MD
  - preservation of SE relation using hydrogen-bond
  - how to connect with usual glass-forming liquids

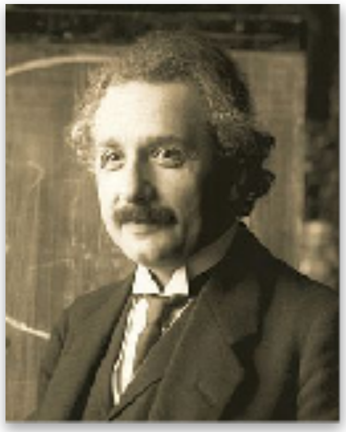
Stokes-Einstein (SE) relation for Brownian motion

Einstein relation

$$D = \frac{k_B T}{\zeta m}$$

Stokes law

$$\zeta^{-1} = \frac{m}{6\pi\eta a}$$



Stokes-Einstein relation

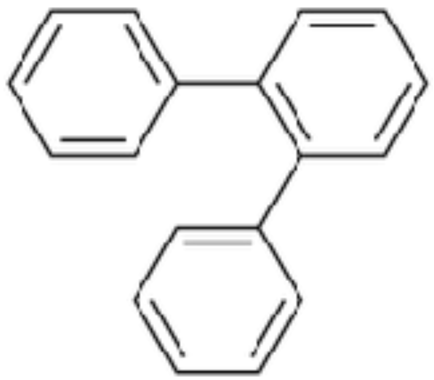
$$D\eta = \frac{k_B T}{6\pi a}$$

$$\frac{D\eta}{T} = \text{const.}$$

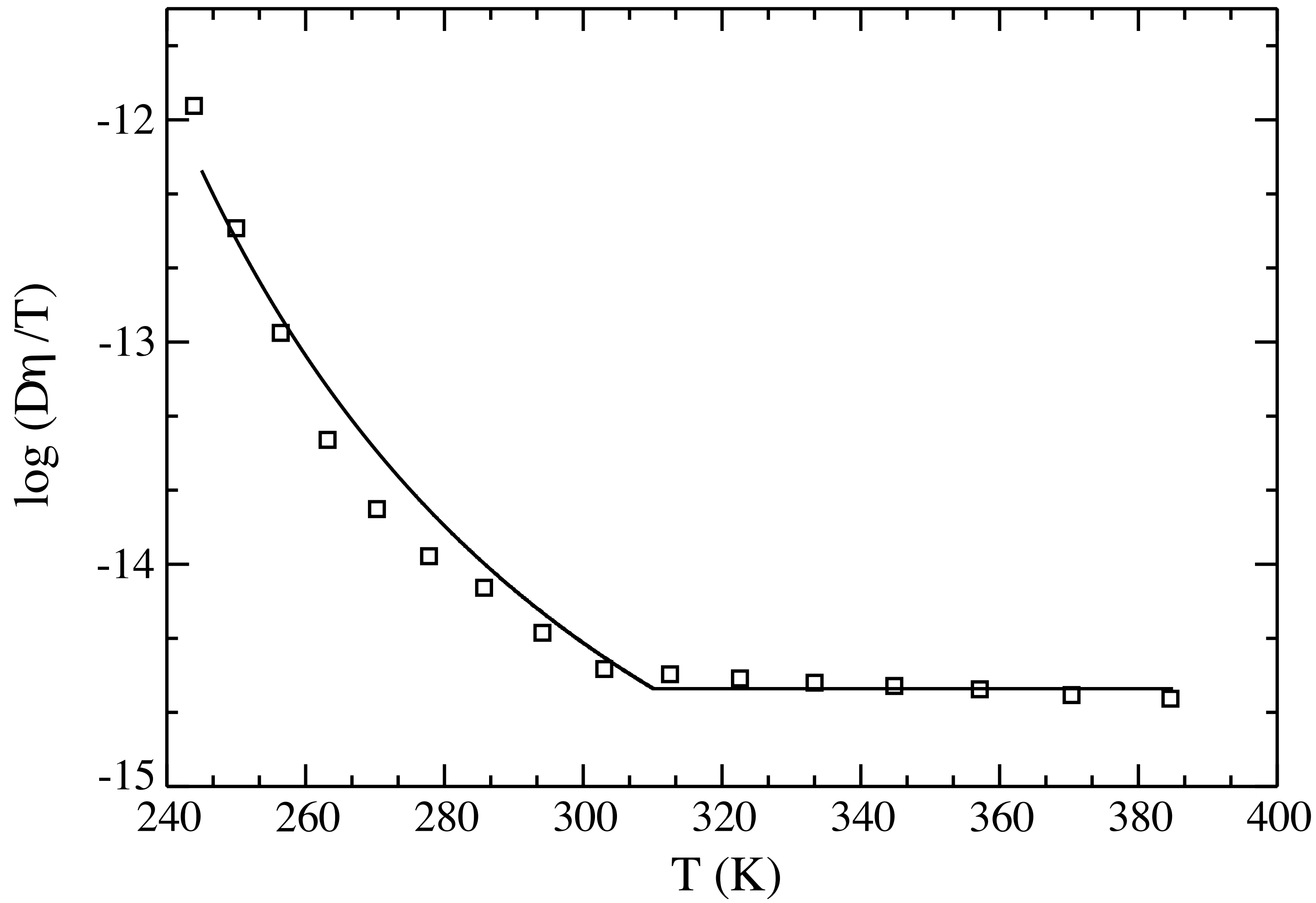
Einstein relation + Stokes's drag force
→ Stokes-Einstein

Molecular-level version of SE relation and its violation

$$\frac{D\eta}{T} = \text{const.}$$



$$T_g = 240\ \text{K}$$

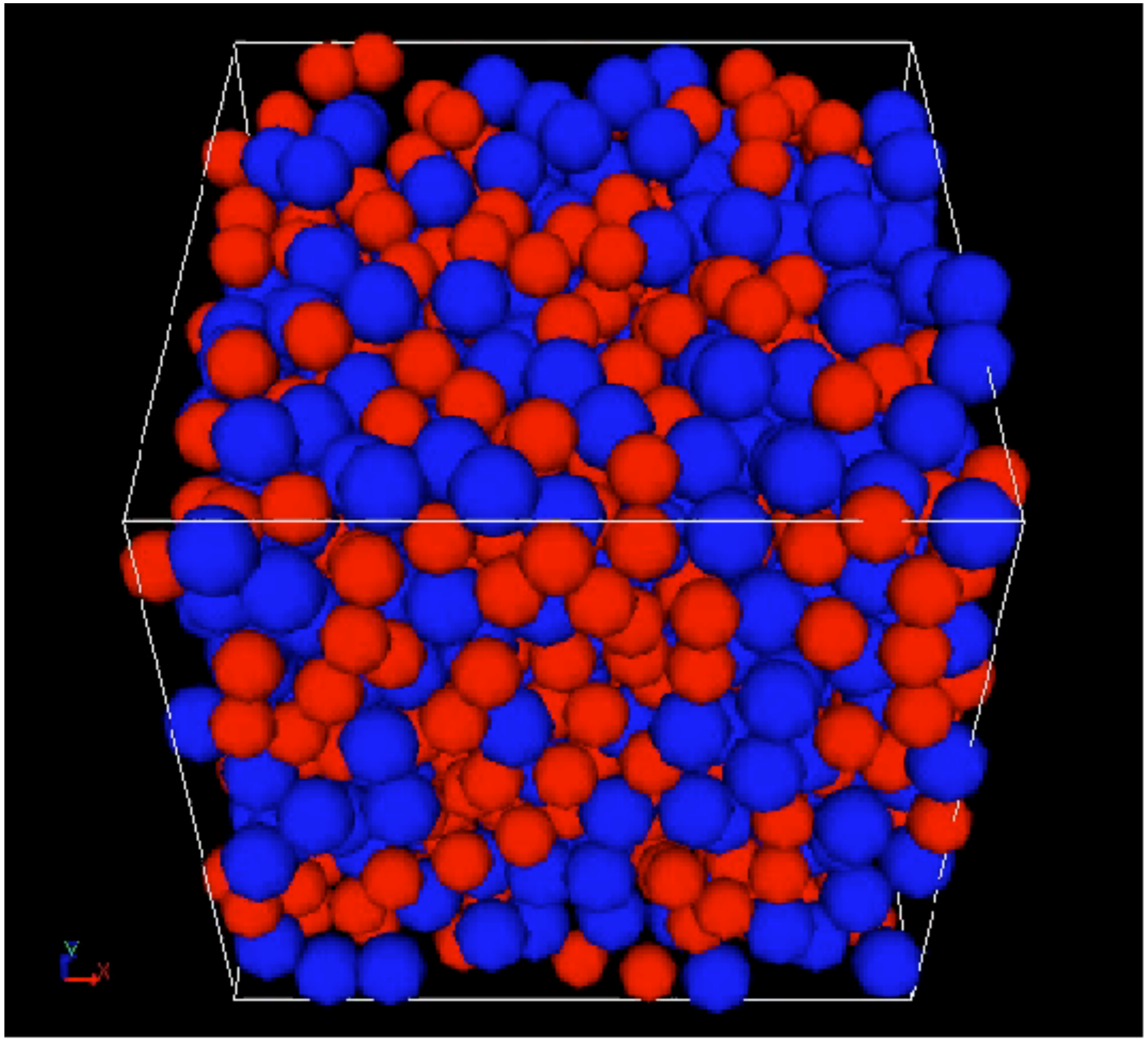


F. Fujara, et al., Z. Phys. B 88, 195 (1992)

S. Merabia and D. Long, Eur. Phys. J. E 9, 195 (2002)

Molecular-level version of SE relation and its violation

$$\frac{D\eta}{T} = \text{const.}$$

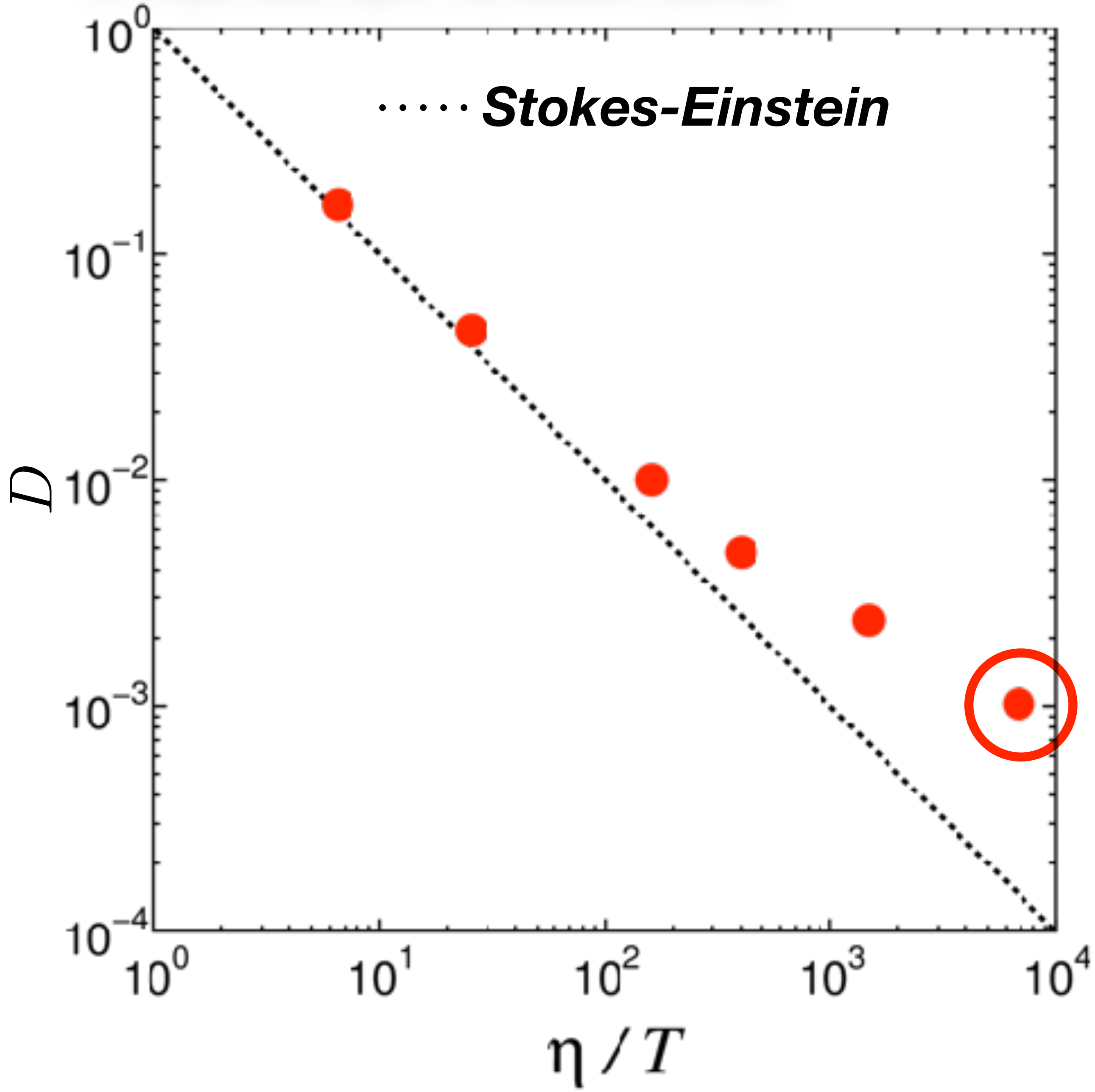


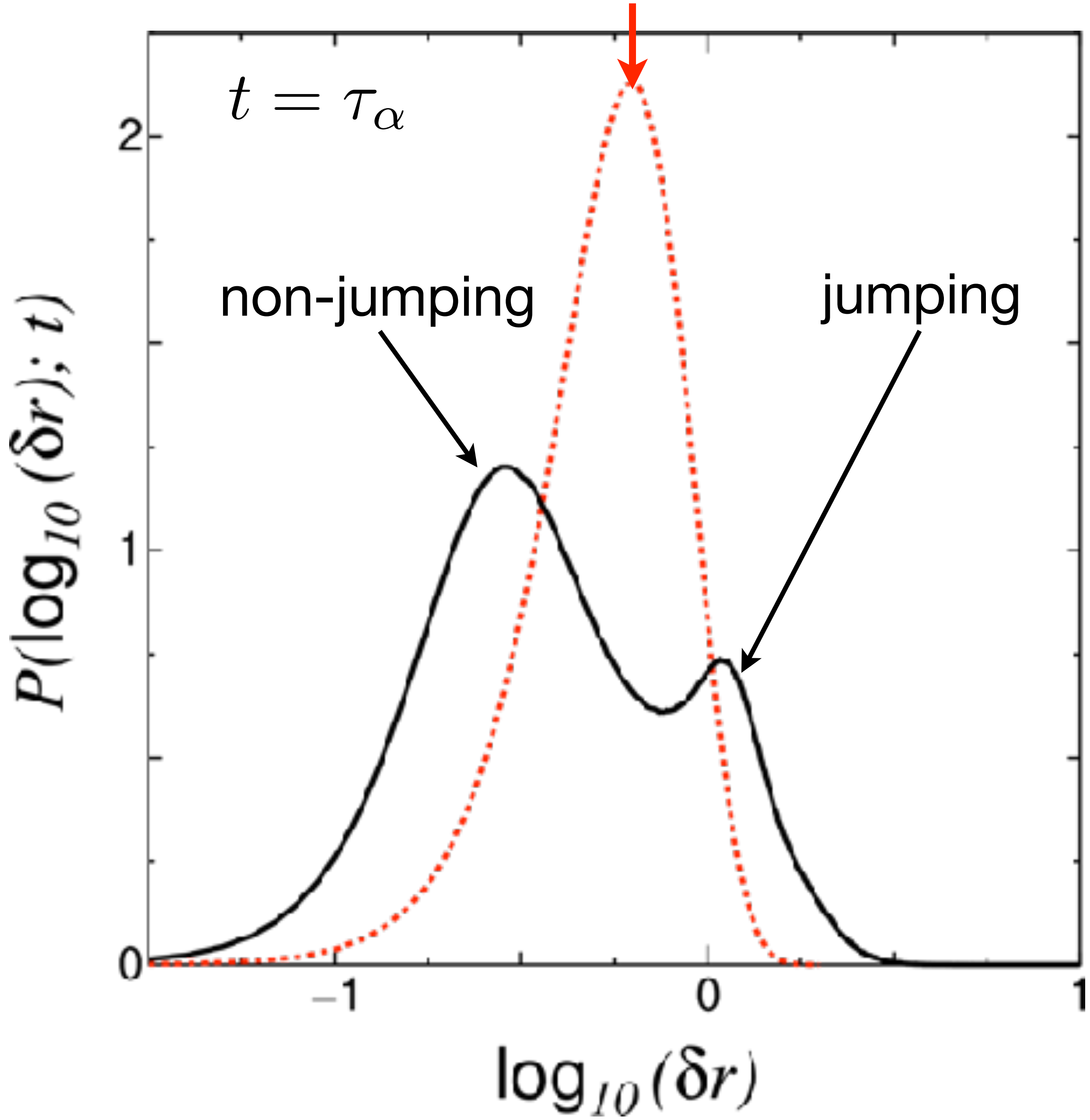
(supercooled state in binary soft-spheres)

Molecular-level version of SE relation and its violation

K. Kim and S. Saito,
J. Phys. Soc. Jpn. 79, 093601 (2010)

$$G_s(\delta r; t) = [1/(4\pi D t)^{3/2}] \exp(-\delta r^2/4Dt)$$





Sign of non-Gaussianity or dynamic heterogeneity?

How to evaluate shear viscosity?

Green-Kubo formula

$$G_{\alpha\beta}(t) = \frac{V}{k_B T}\langle \sigma_{\alpha\beta}(t)\sigma_{\alpha\beta}(0)\rangle$$

$$\eta = \int_0^\infty G_\eta(t)dt \qquad (G_\eta(t) = (G_{xy}(t) + G_{xz}(t) + G_{yz}(t))/3)$$

Due to heavy computations of $\boldsymbol{\eta}$,
a time scale $\boldsymbol{\tau}$ is used for characterizing $\boldsymbol{\eta}$

Z. Shi, P. G. Debenedetti and F. H. Stillinger, J. Chem. Phys. 138, 12A526 (2013)

Scenario① : Maxwell viscoelastic model

Viscoelasticity: Maxwell model

$$G_\eta(t) = G_\infty \exp(-t/\tau_M)$$

$$\eta = \int_0^\infty G_\infty \exp(-t/\tau_M)dt = G_\infty \tau_M$$

Maxwell time : $\tau_M = \eta/G_\infty$

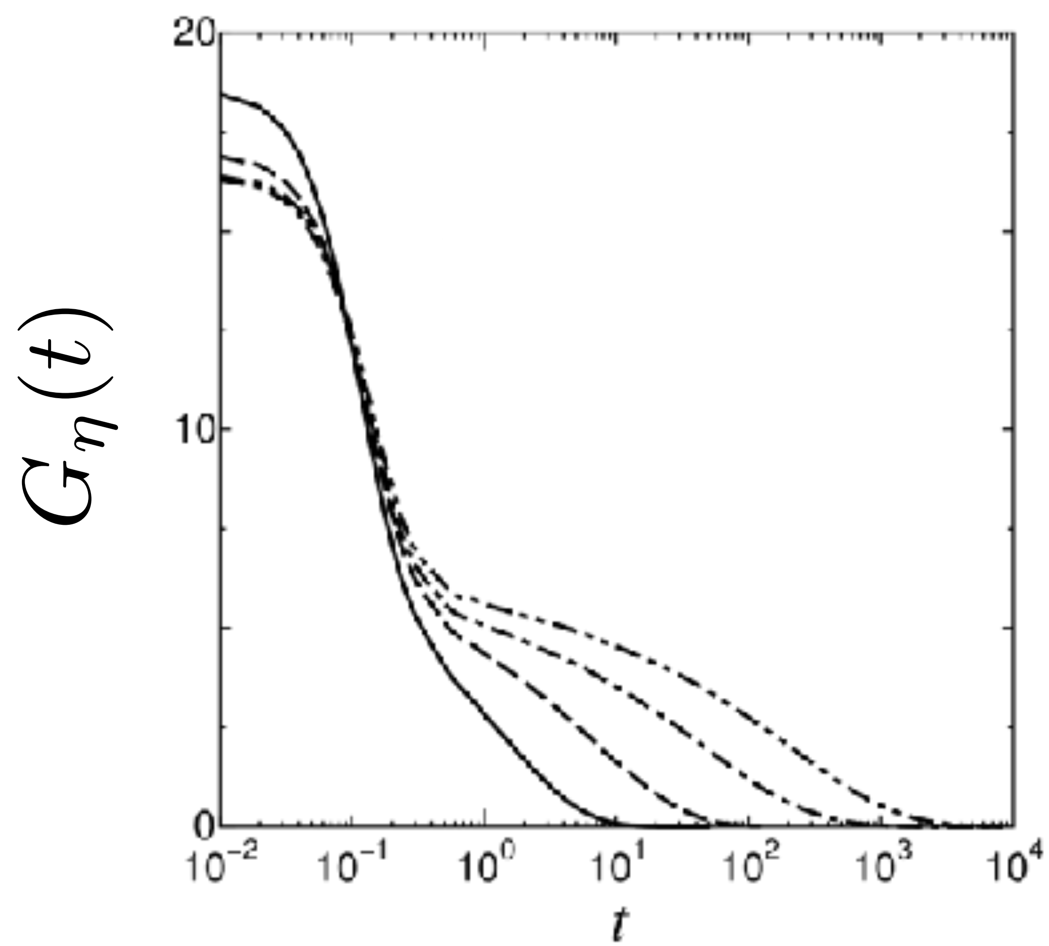
instantaneous shear modulus : G_∞

SE relation

$$G_\infty = G_\eta(0) = \text{const.}$$

$$D\eta/T \propto D\tau_M/T$$

(binary soft-spheres)



Scenario② : Gauss approximation

Gauss approximation

$$F_s(k,t) = \frac{1}{N}\langle \rho_k(t)\rho_{-k}(0)\rangle$$
$$= \exp(-Dk^2 t) = \exp(-t/\tau_\alpha)$$

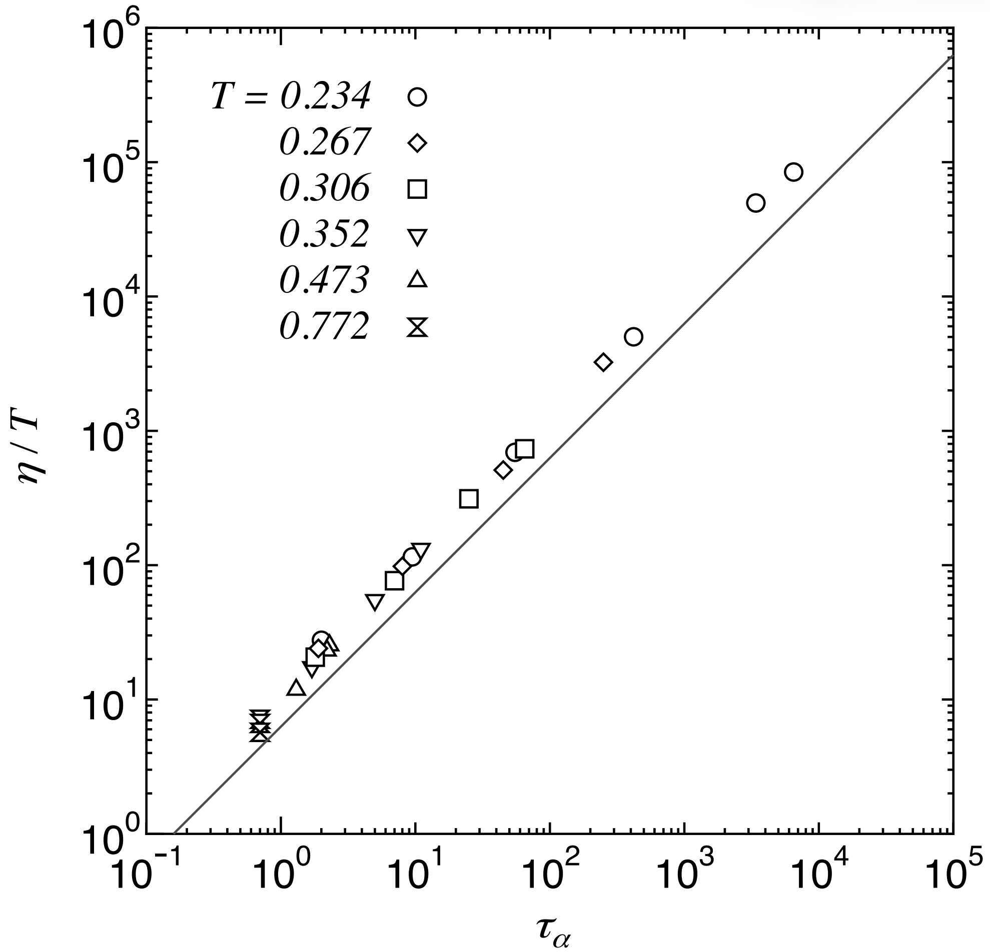
$$D \propto 1/\tau_\alpha$$

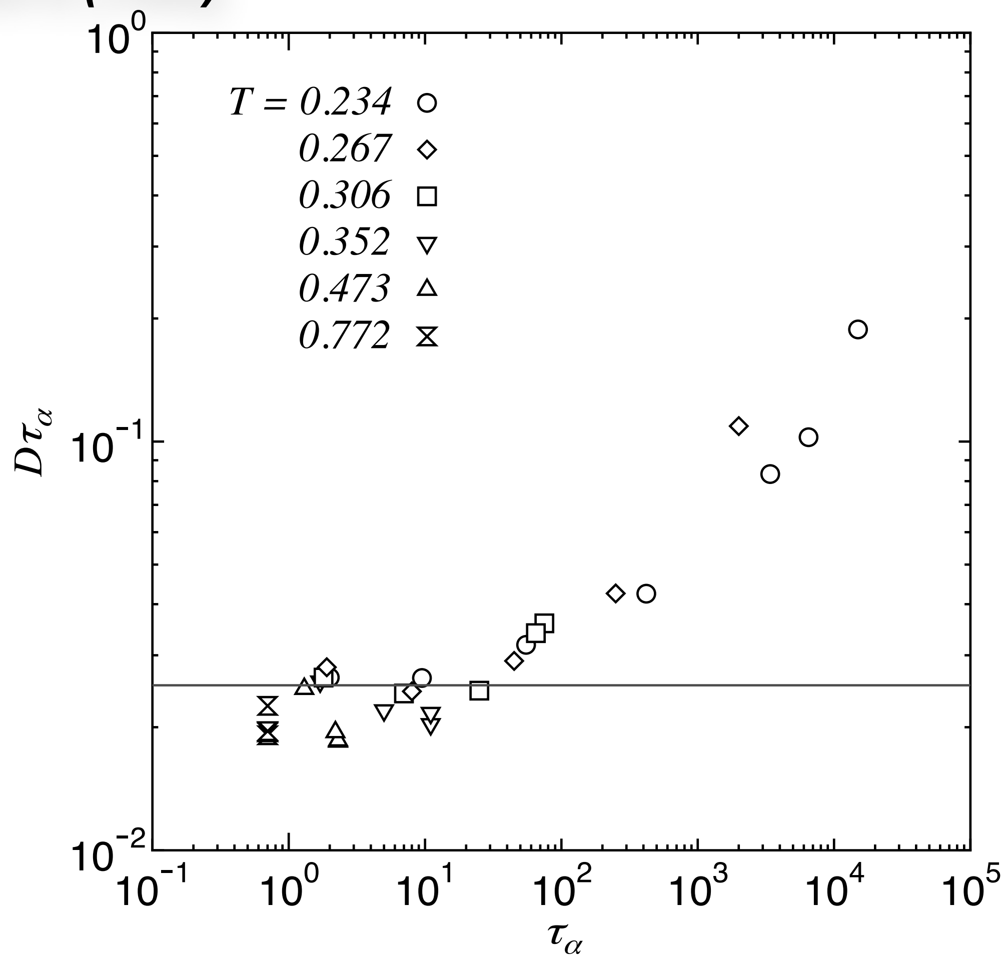
SE relation

$$\eta/T \propto \tau_\alpha$$

$$D\eta/T \propto D\tau_\alpha$$

(binary soft-spheres) ***R. Yamamoto and A. Onuki, Phys. Rev. Lett. 81, 4915 (1998)***





fractional Stokes-Einstein relation

fractional Stokes-Einstein

$$D \sim (\eta/T)^{-1}$$

$$D \sim (\eta/T)^{-\zeta}$$

Scenario① : Maxwell model

$$D\eta/T \propto D\tau/T$$

$$D \sim (\tau/T)^{-\zeta}$$

Scenario② : Gauss approximation

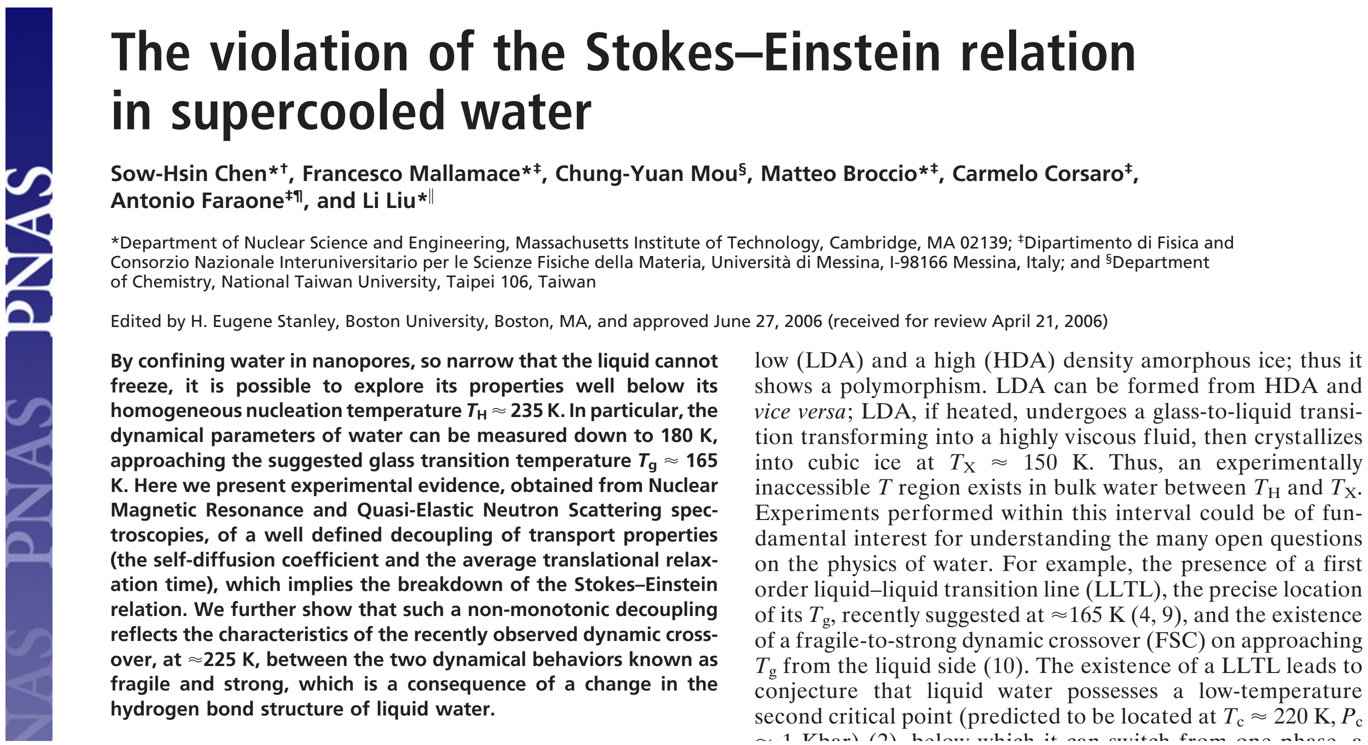
$$D\eta/T \propto D\tau$$

$$D \sim \tau^{-\zeta}$$

$\zeta < 1$: fractional Stokes-Einstein

But, τ is τ_M or τ_α? What is the physical implication ?

Fragile-Strong crossover and violation of SE are evidences of liquid-liquid transition ?



PNAS

The violation of the Stokes–Einstein relation in supercooled water

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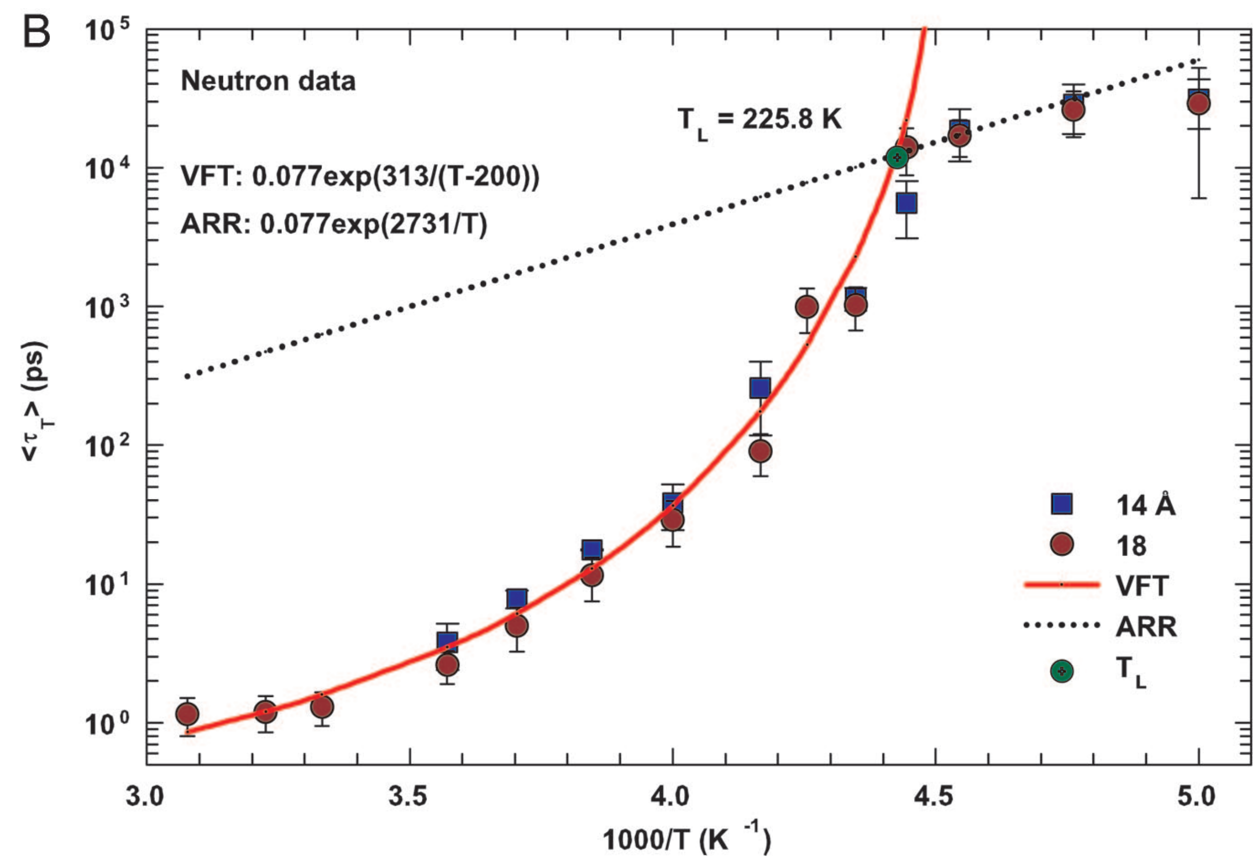
Edited by H. Eugene Stanley, Boston University, Boston, MA, and approved June 27, 2006 (received for review April 21, 2006)

By confining water in nanopores, so narrow that the liquid cannot freeze, it is possible to explore its properties well below its homogeneous nucleation temperature $T_H \approx 235$ K. In particular, the dynamical parameters of water can be measured down to 180 K, approaching the suggested glass transition temperature $T_g \approx 165$ K. Here we present experimental evidence, obtained from Nuclear Magnetic Resonance and Quasi-Elastic Neutron Scattering spectroscopies, of a well defined decoupling of transport properties (the self-diffusion coefficient and the average translational relaxation time), which implies the breakdown of the Stokes–Einstein relation. We further show that such a non-monotonic decoupling reflects the characteristics of the recently observed dynamic crossover, at ≈225 K, between the two dynamical behaviors known as fragile and strong, which is a consequence of a change in the hydrogen bond structure of liquid water.

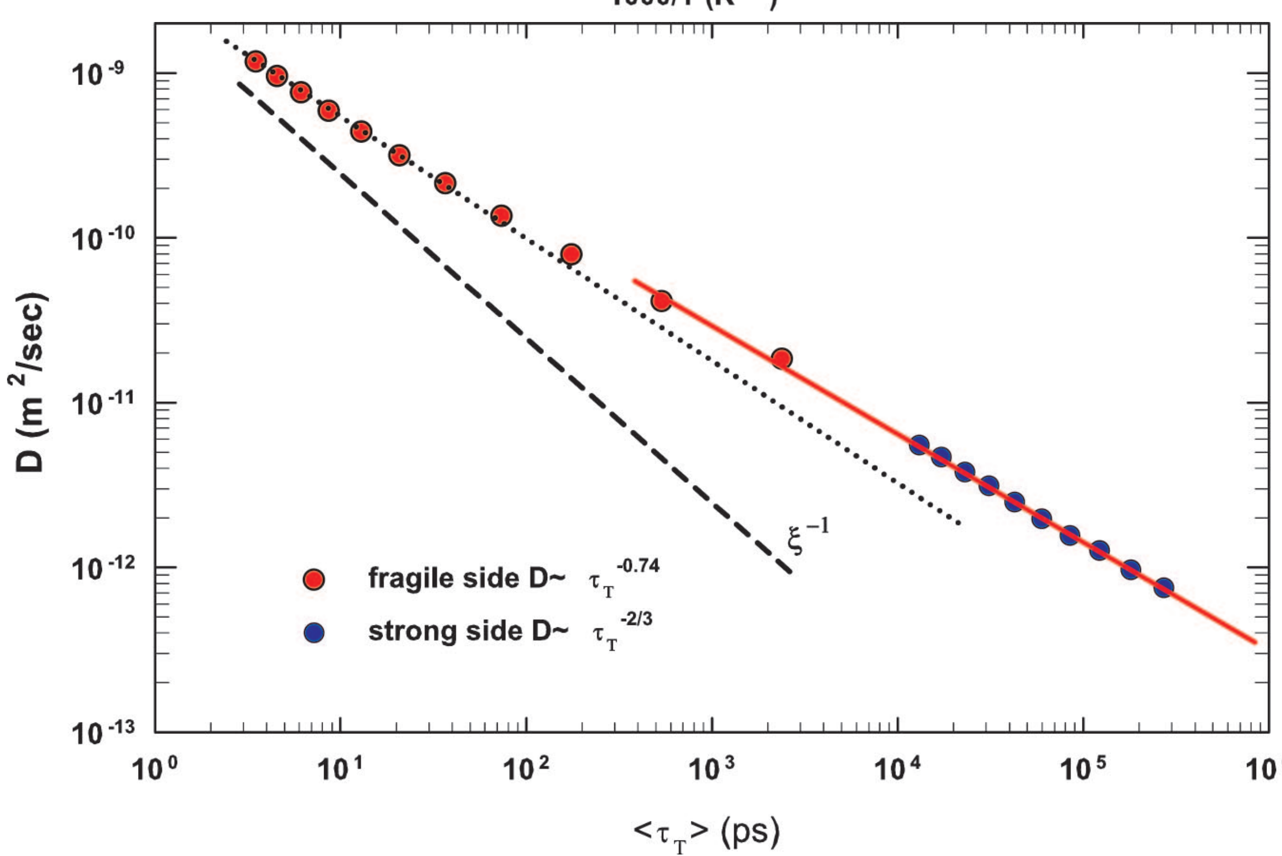
low (LDA) and a high (HDA) density amorphous ice; thus it shows a polymorphism. LDA can be formed from HDA and *vice versa*; LDA, if heated, undergoes a glass-to-liquid transition transforming into a highly viscous fluid, then crystallizes into cubic ice at $T_X \approx 150$ K. Thus, an experimentally inaccessible T region exists in bulk water between T_H and T_X. Experiments performed within this interval could be of fundamental interest for understanding the many open questions on the physics of water. For example, the presence of a first order liquid–liquid transition line (LLTL), the precise location of its T_g, recently suggested at ≈165 K (4, 9), and the existence of a fragile-to-strong dynamic crossover (FSC) on approaching T_g from the liquid side (10). The existence of a LLTL leads to conjecture that liquid water possesses a low-temperature second critical point (predicted to be located at $T_c \approx 220$ K, P_c

Nanoconfined water (experiment)
S.H. Chen, et al., PNAS 103, 12974 (2006)



Scenario② : Gauss approximation

$$D \sim {\tau_\alpha}^{-2/3}$$



Fragile-Strong crossover and violation of SE are evidences of liquid-liquid transition ?

nature physics
LETTERS
PUBLISHED ONLINE: 5 JULY 2009 | DOI: 10.1038/NPHYS1328

Appearance of a fractional Stokes–Einstein relation in water and a structural interpretation of its onset

Limei Xu[1,2], Francesco Mallamace[3]*, Zhenyu Yan[2], Francis W. Starr[4], Sergey V. Buldyrev[2,5] and H. Eugene Stanley[2]*

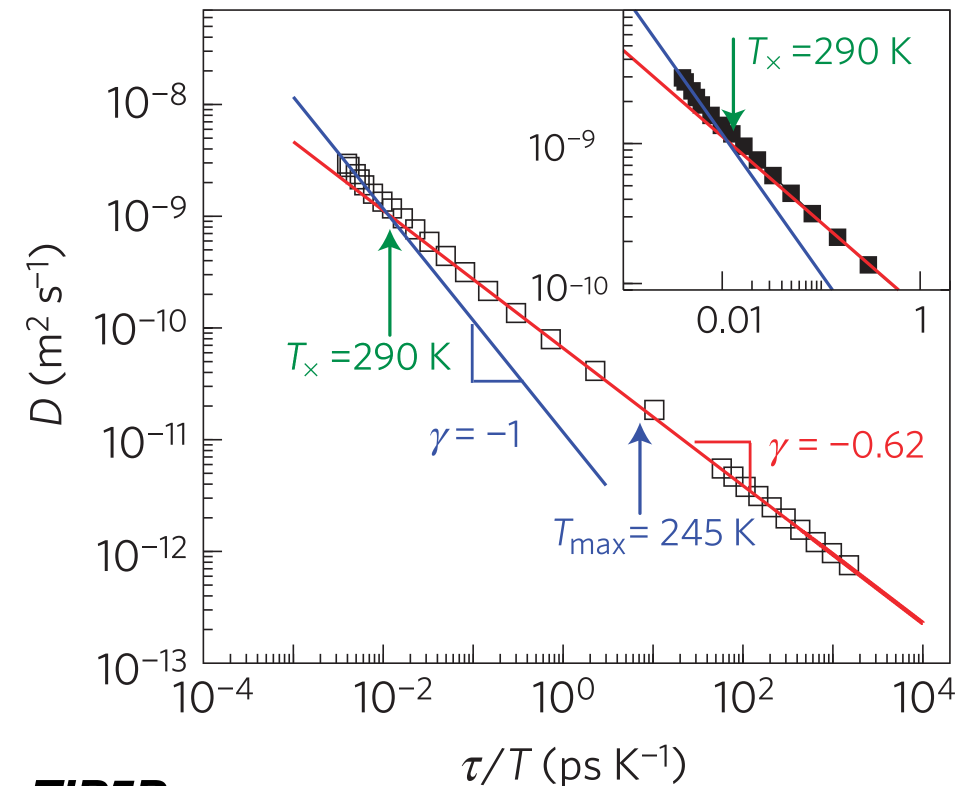
Nanoconfined water (experiment) and TIP5P(MD)
L. Xu, et al., Nat. Phys. 5, 565 (2009)

Scenario① : Maxwell model

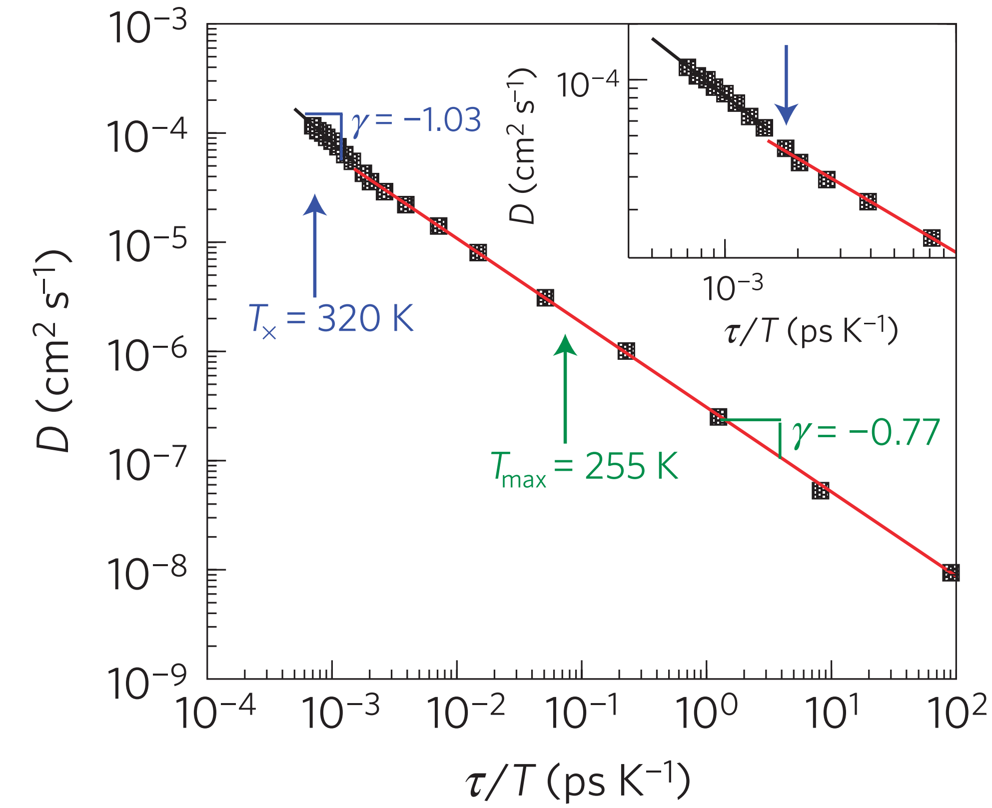
$$D \sim (\tau_\alpha/T)^{-0.62}$$

$$(\tau_\alpha \sim \tau_M???)$$

Nanoconfined water



TIP5P

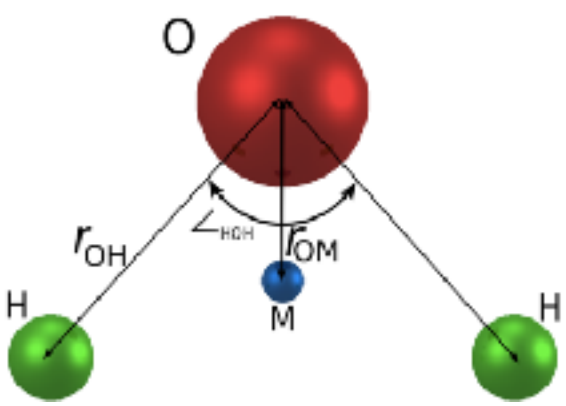


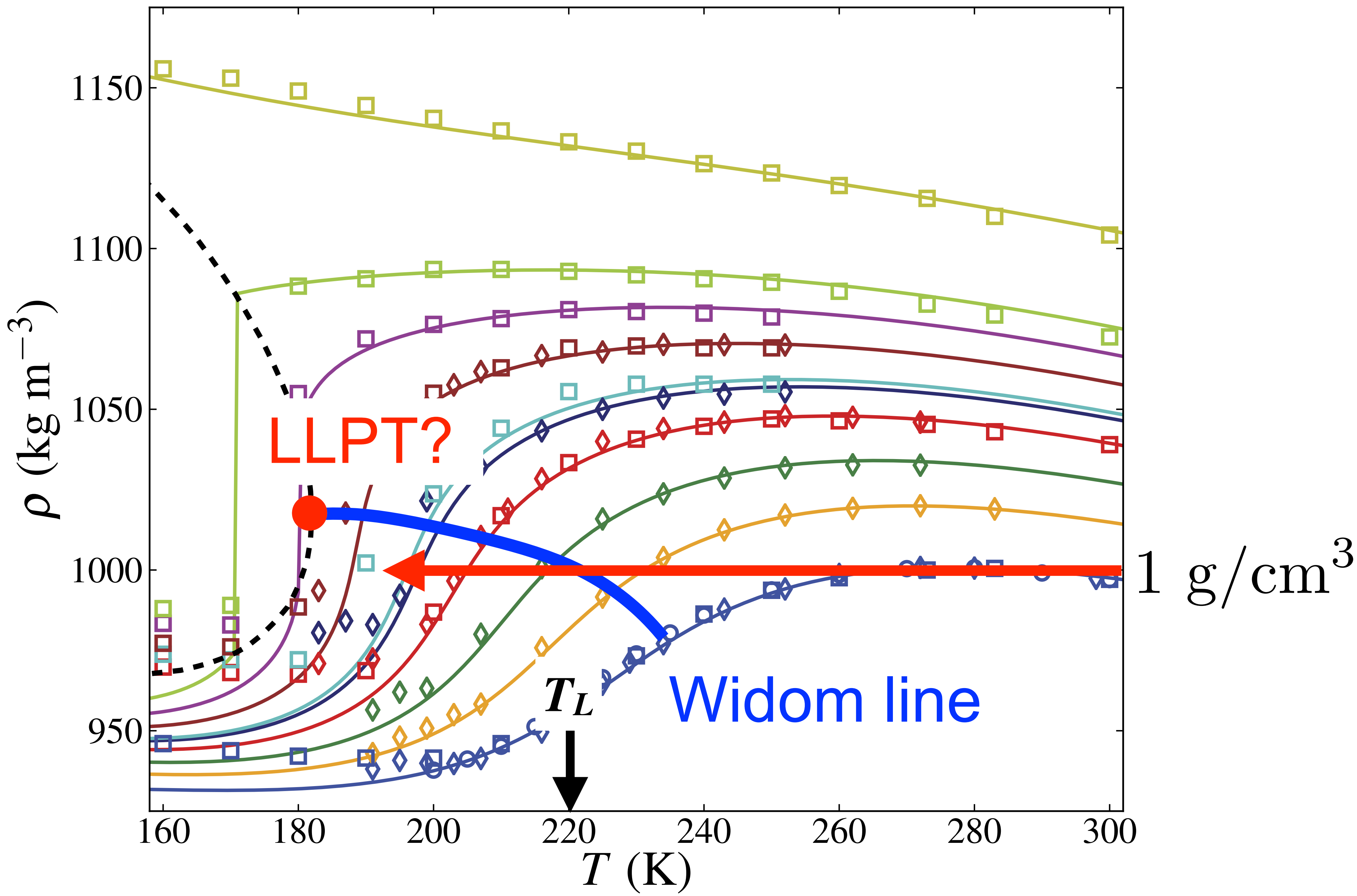
Whatever, why SE breakdowns in supercooled water?

- Key point: direct calculations of viscosity in MD
- Strict assessment of SE violation
  - Maxwell model vs. Gauss approximation
- We newly propose preservation of SE relation
  - hydrogen-bond lifetime
  - non-Gaussianity and non-exponentiality

Phase diagram of TIP4P/2005 supercooled water

isobars





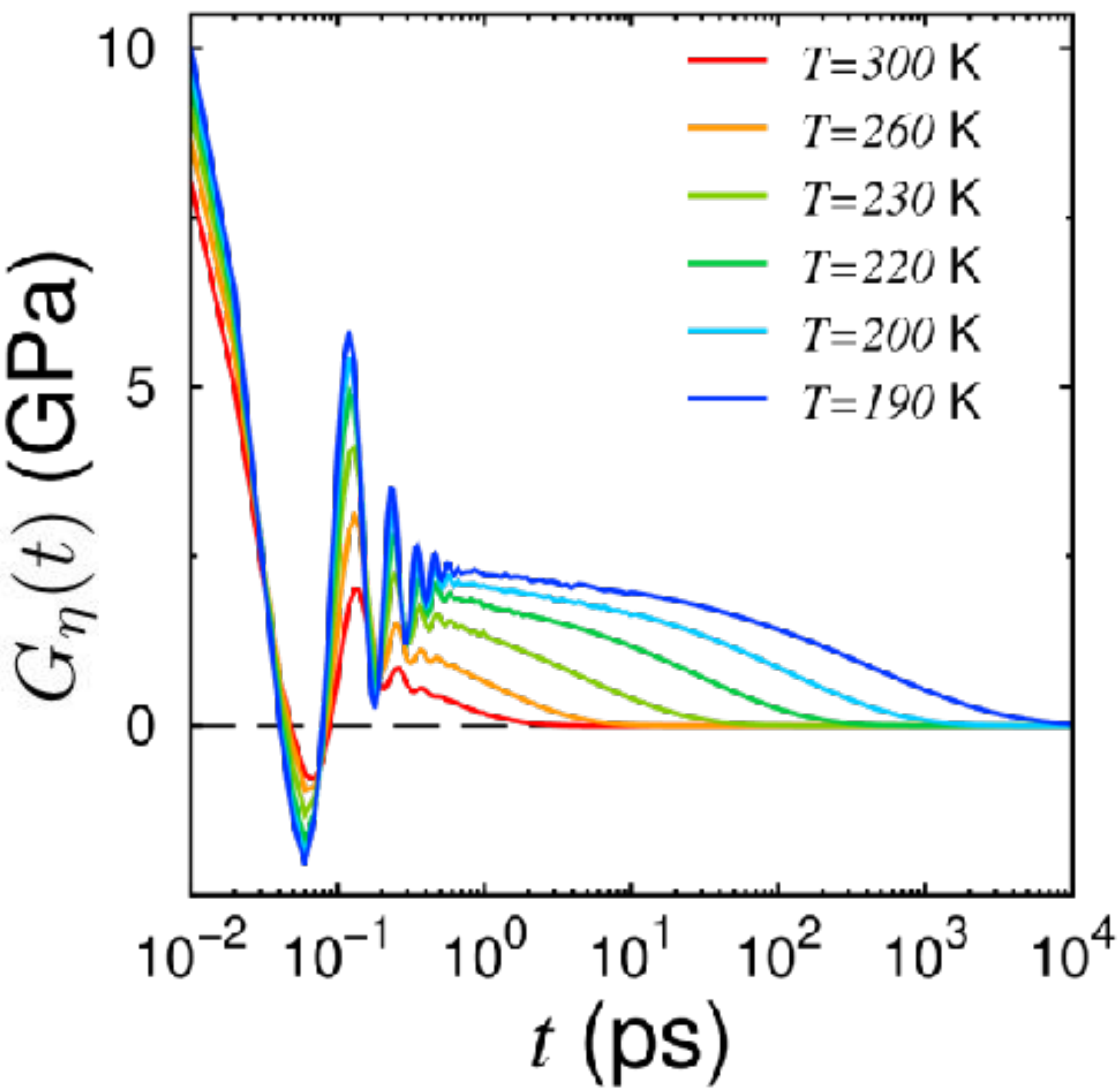
R. S. Singh, J. W. Biddle, P. G. Debenedetti, and M. A. Anisimov, J. Chem. Phys. 144, 144504 (2016)

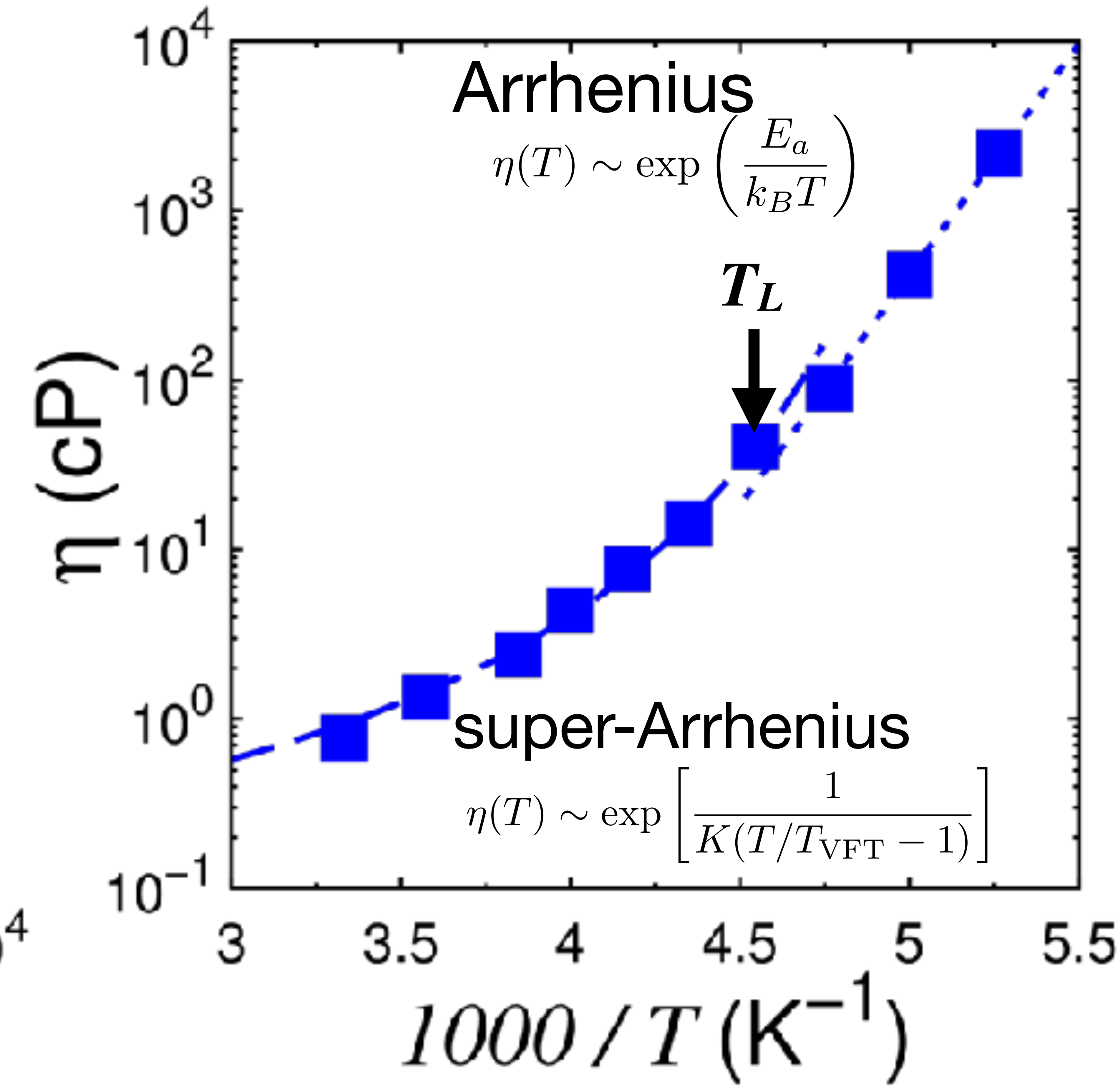
TIP4P/2005

stress correlation

$$\eta = \int_0^\infty G_\eta(t)dt$$

viscosity

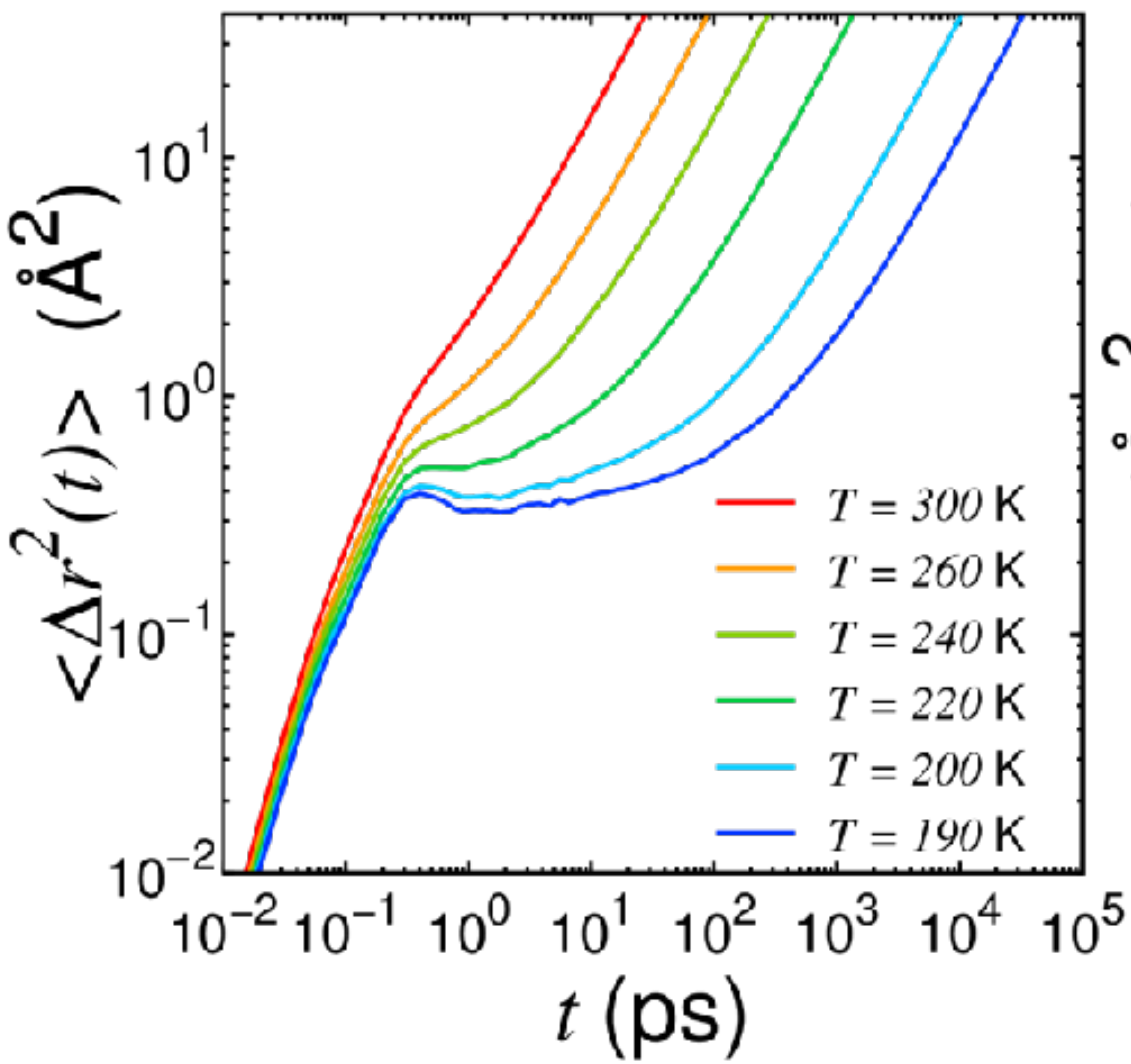




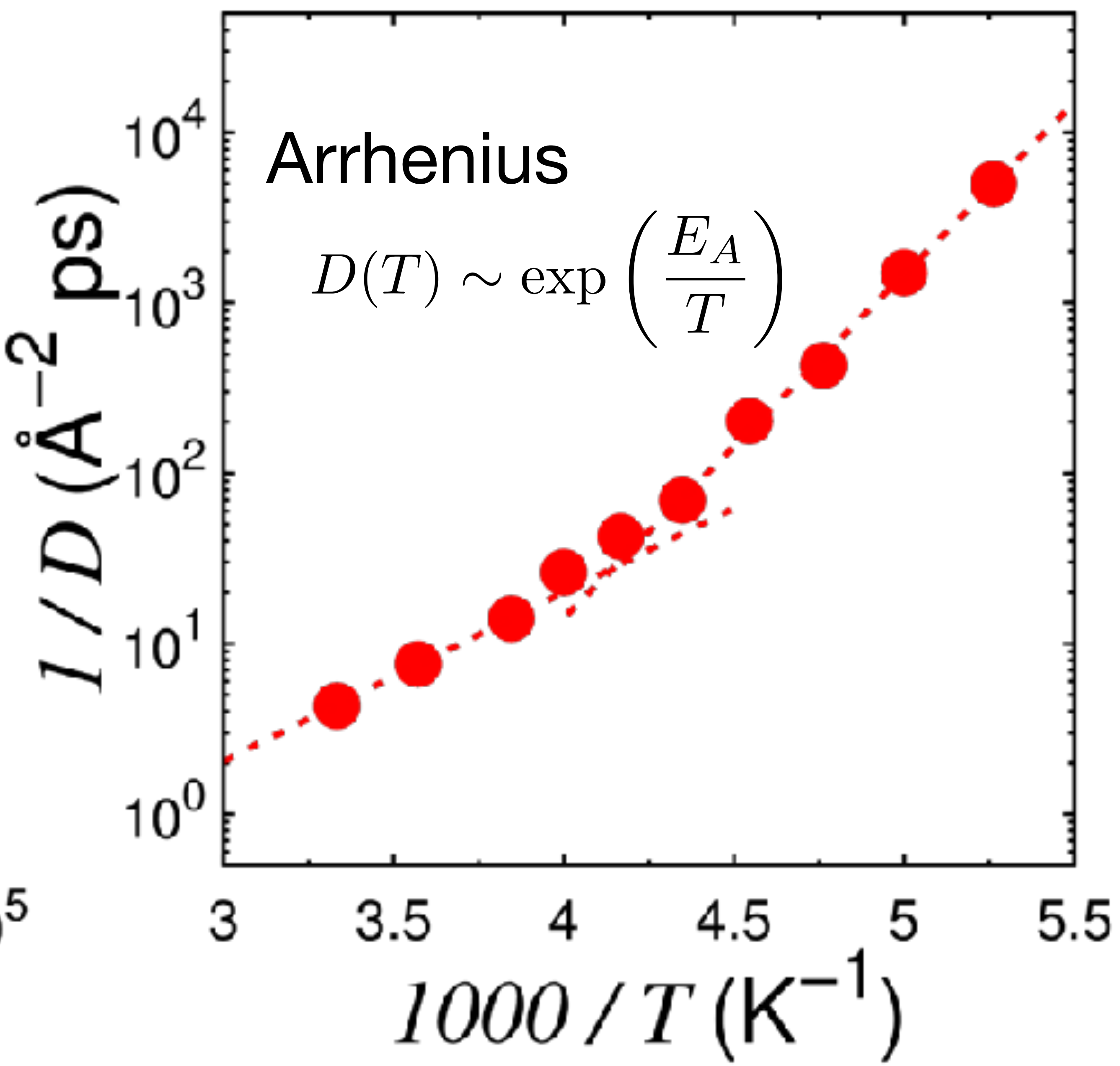
fragile-strong crossover: $T_L \approx 220\mathrm{K}$

TIP4P/2005

MSD $D = \lim_{t \to \infty} \frac{1}{6t} \langle |\boldsymbol{r}(t) - \boldsymbol{r}(0)|^2 \rangle$

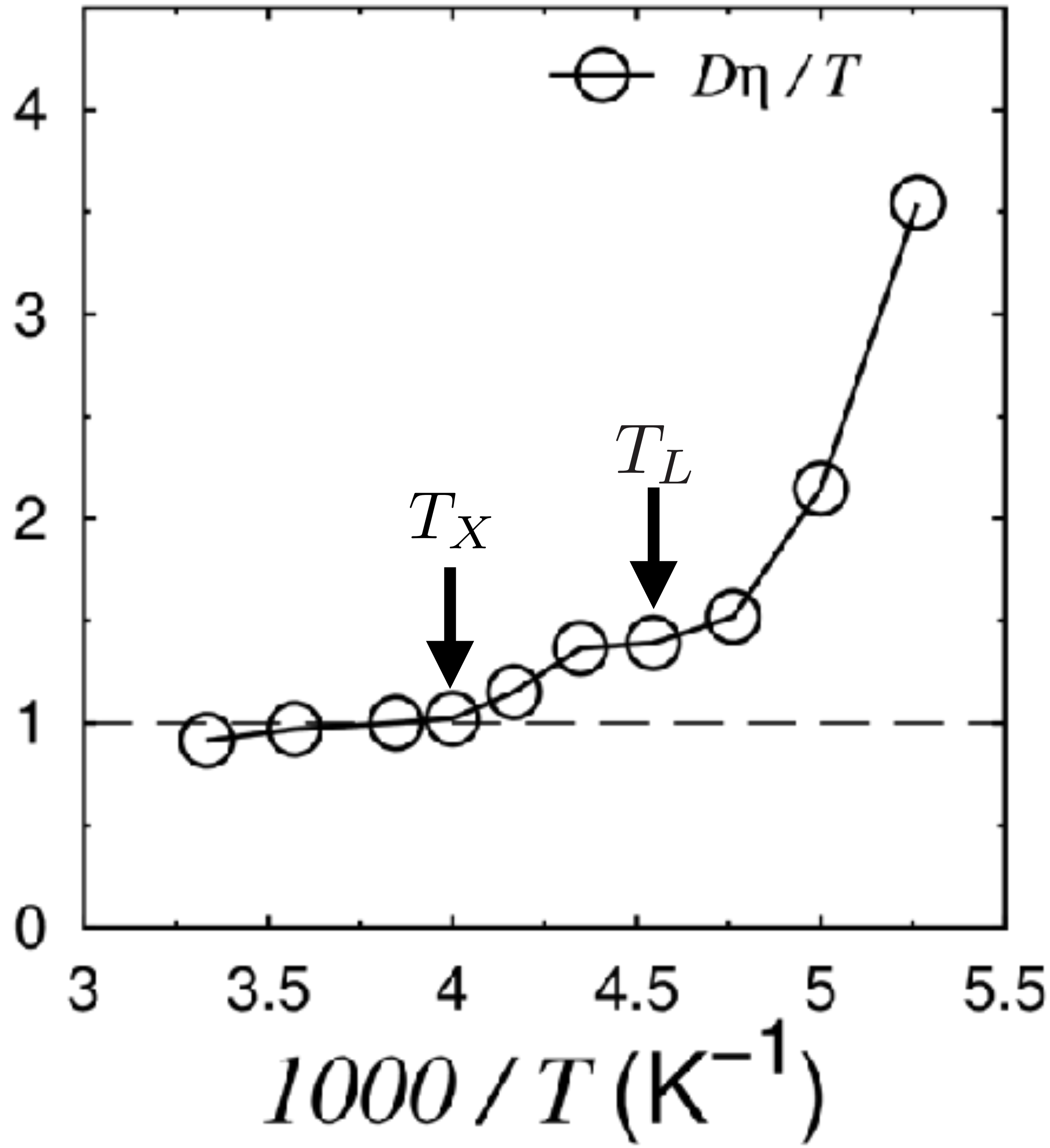


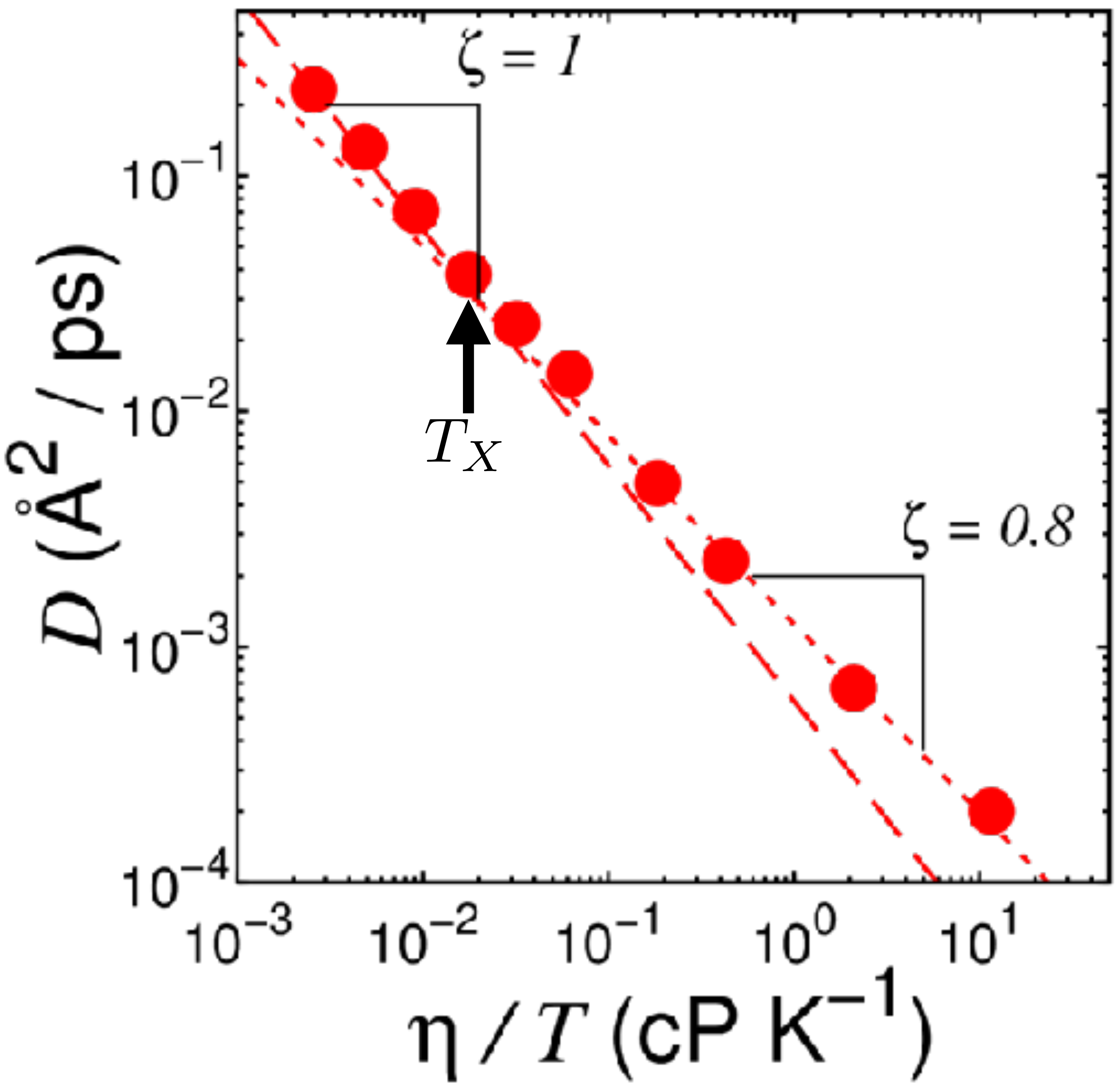
self-diffusion



No obvious fragile-strong crossover!!

Stokes-Einstein relation

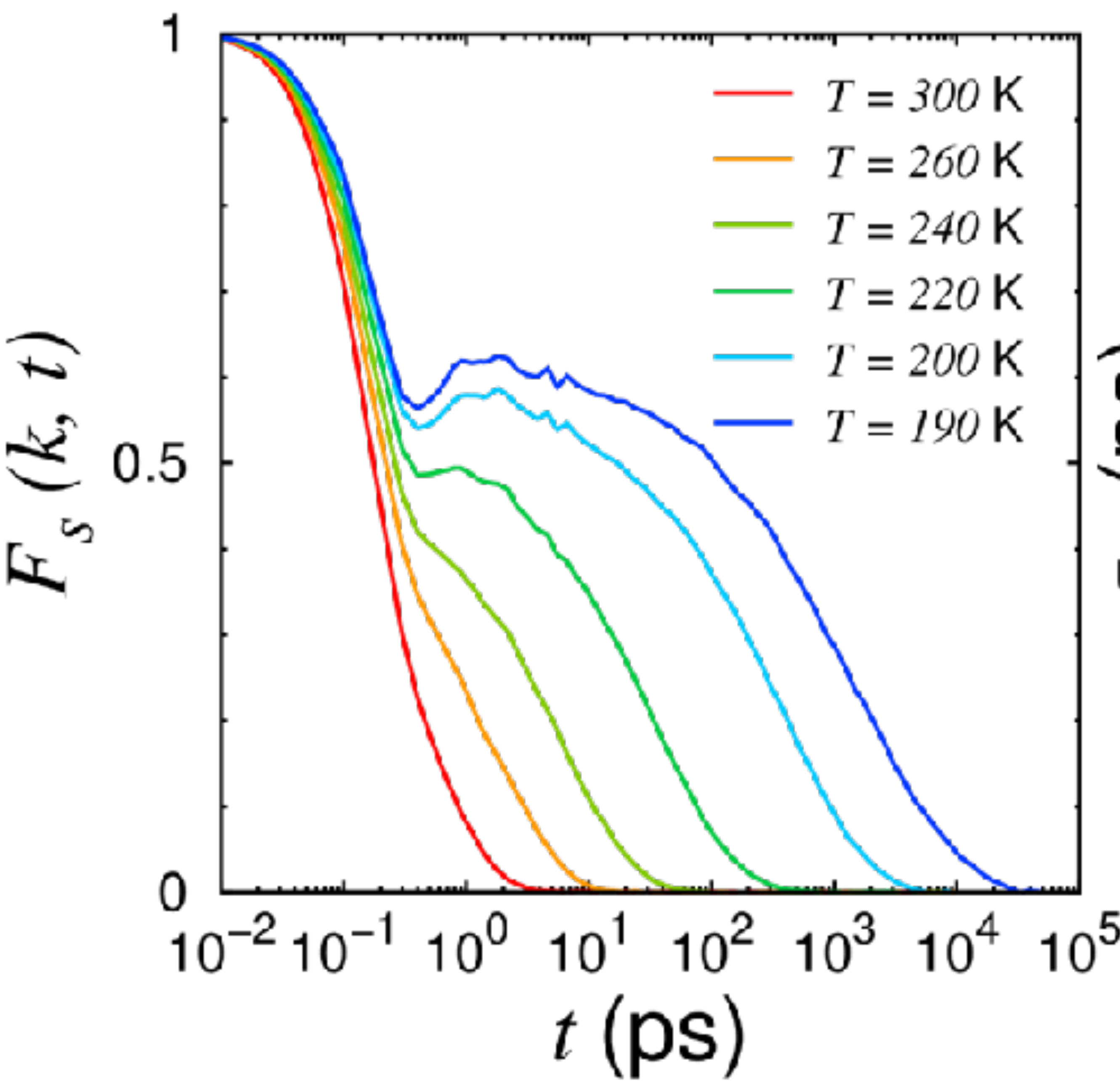


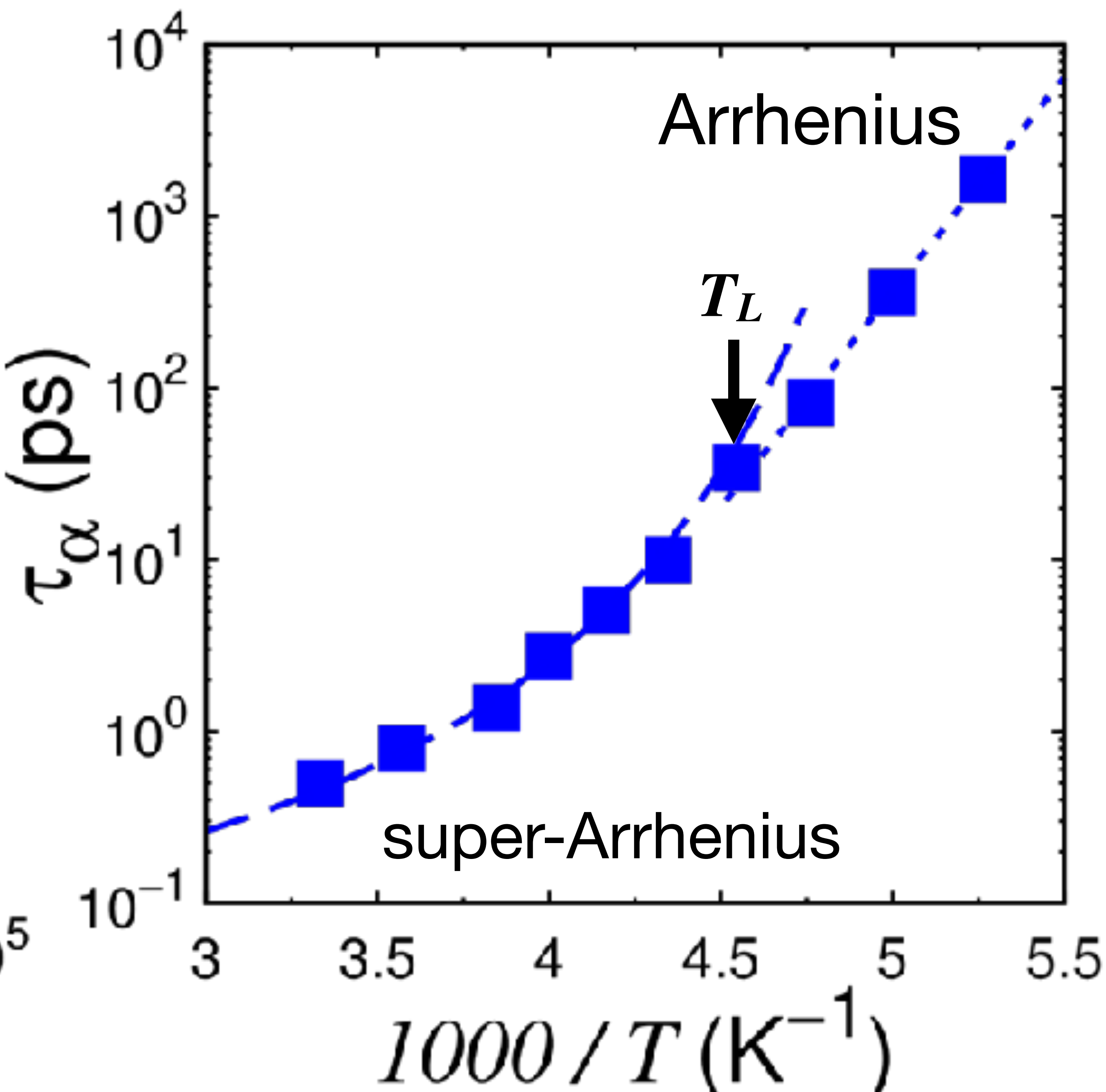


Onset temperature of SE violation: $T_L \approx 220\mathrm{K}$?

TIP4P/2005

density correlation $F(\boldsymbol{k}, t) = \langle \rho_k(t) \rho_{-k}(0) \rangle$ structural relaxation time

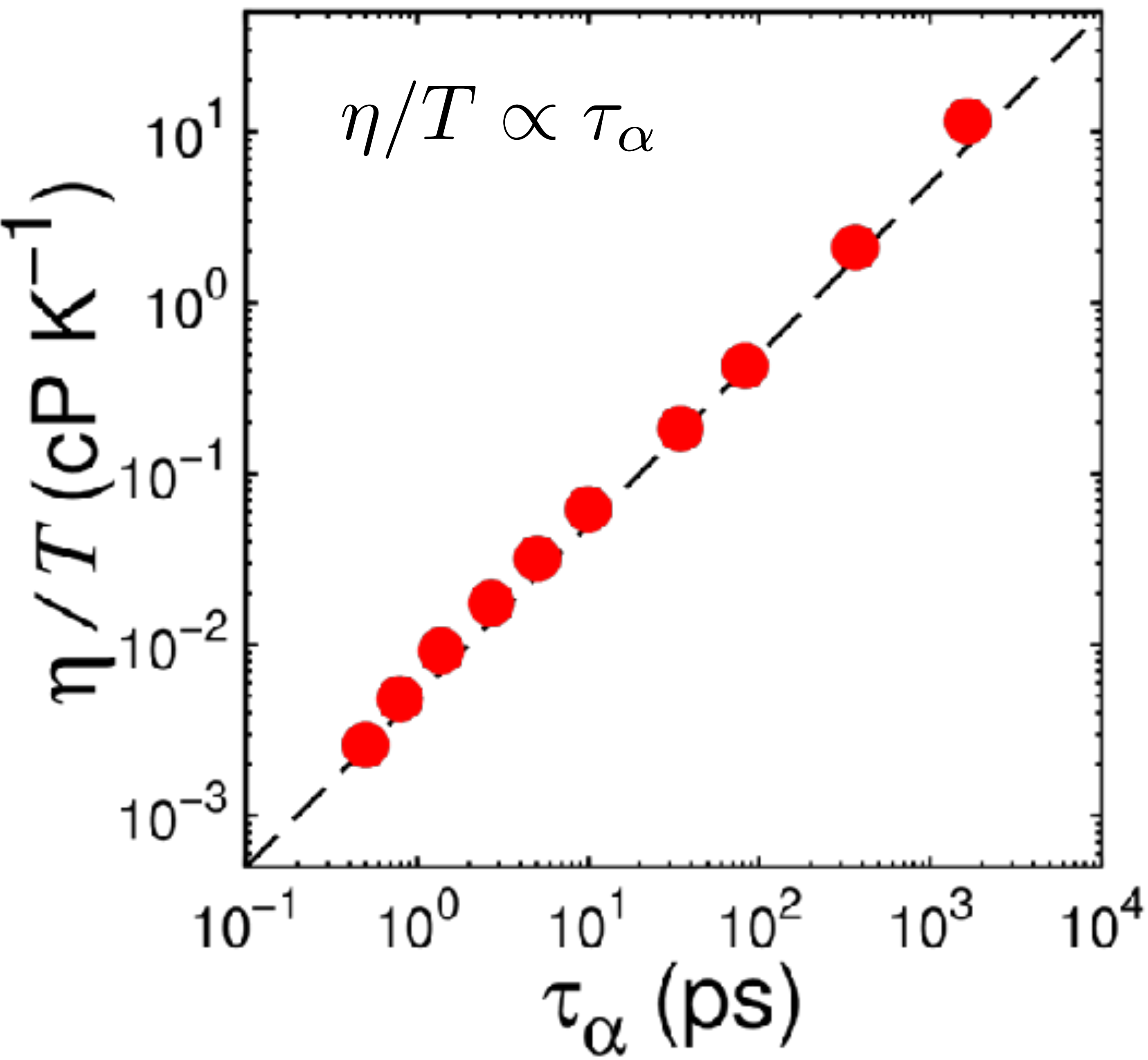


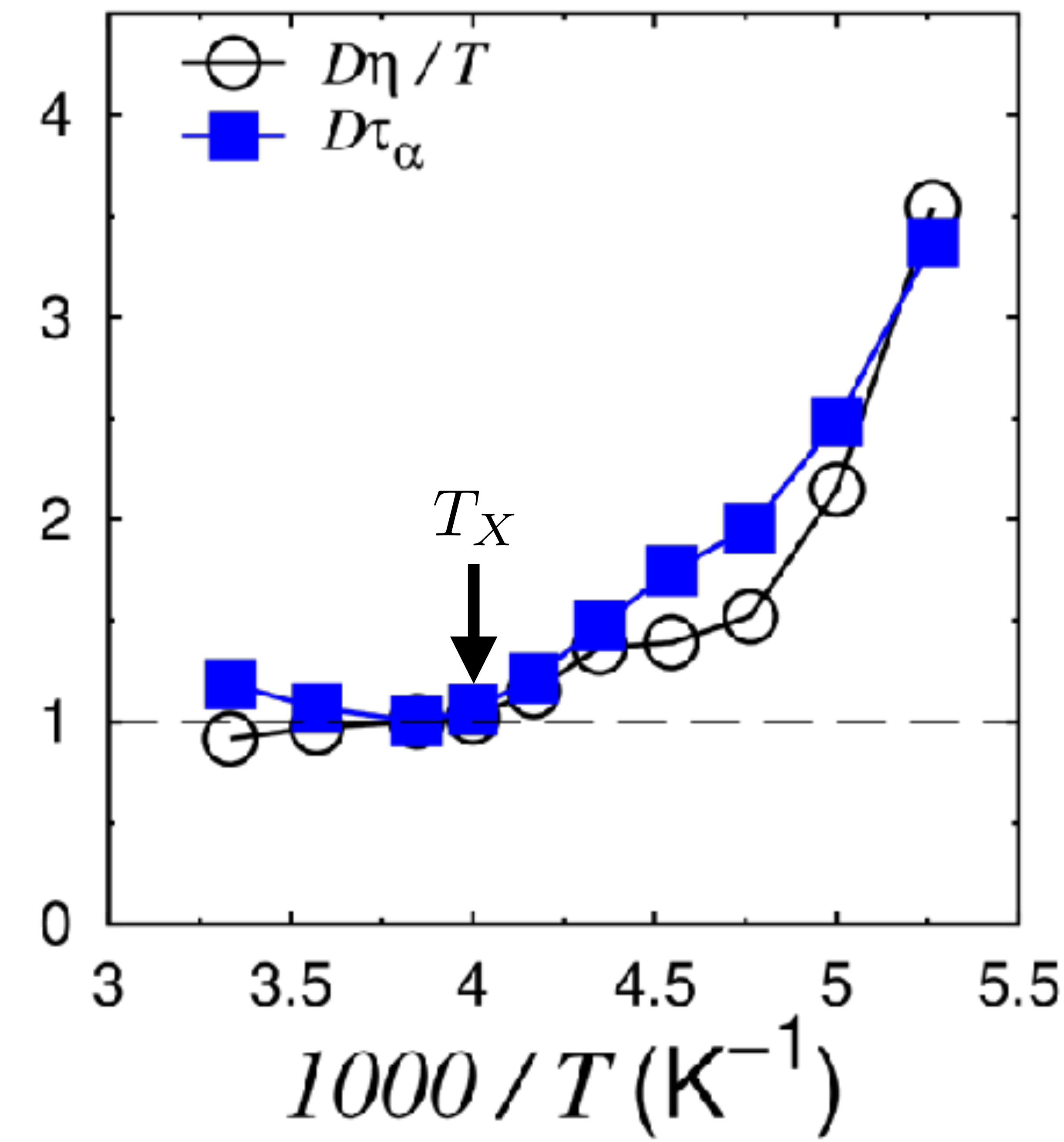


fragile-strong crossover: $T_L \approx 220\mathrm{K}$

Gauss approximation or Maxwell model?

$$D\eta/T \sim D\tau_\alpha \neq \text{const}$$

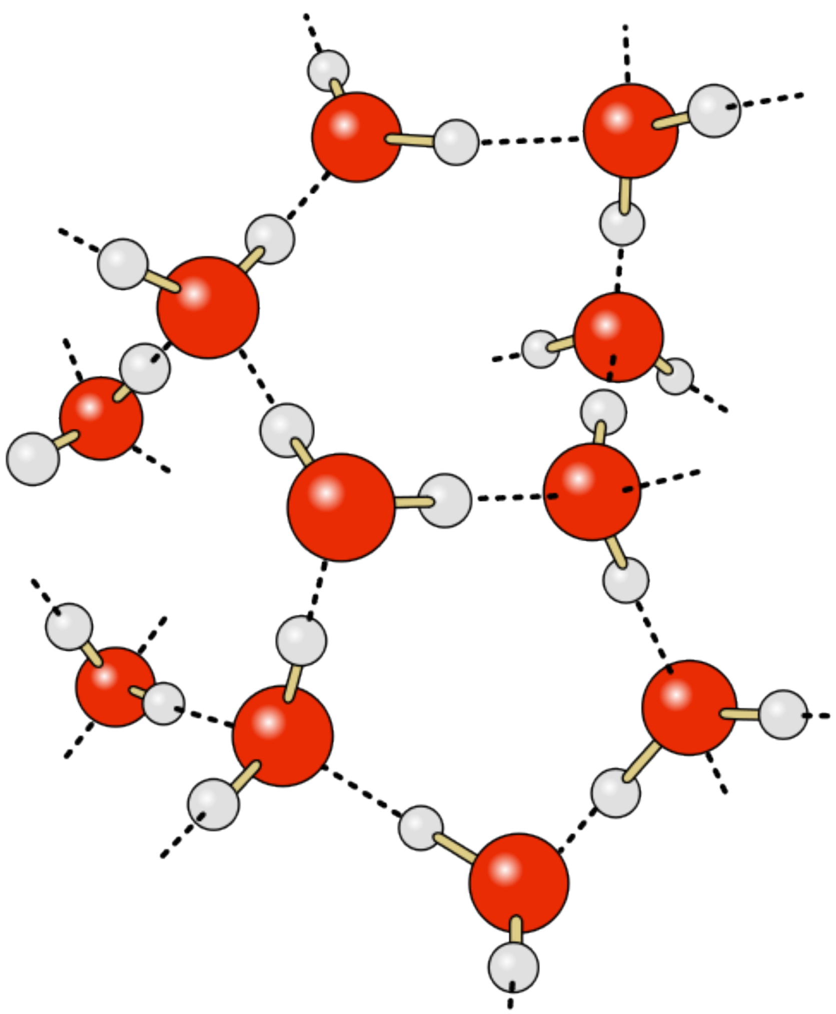




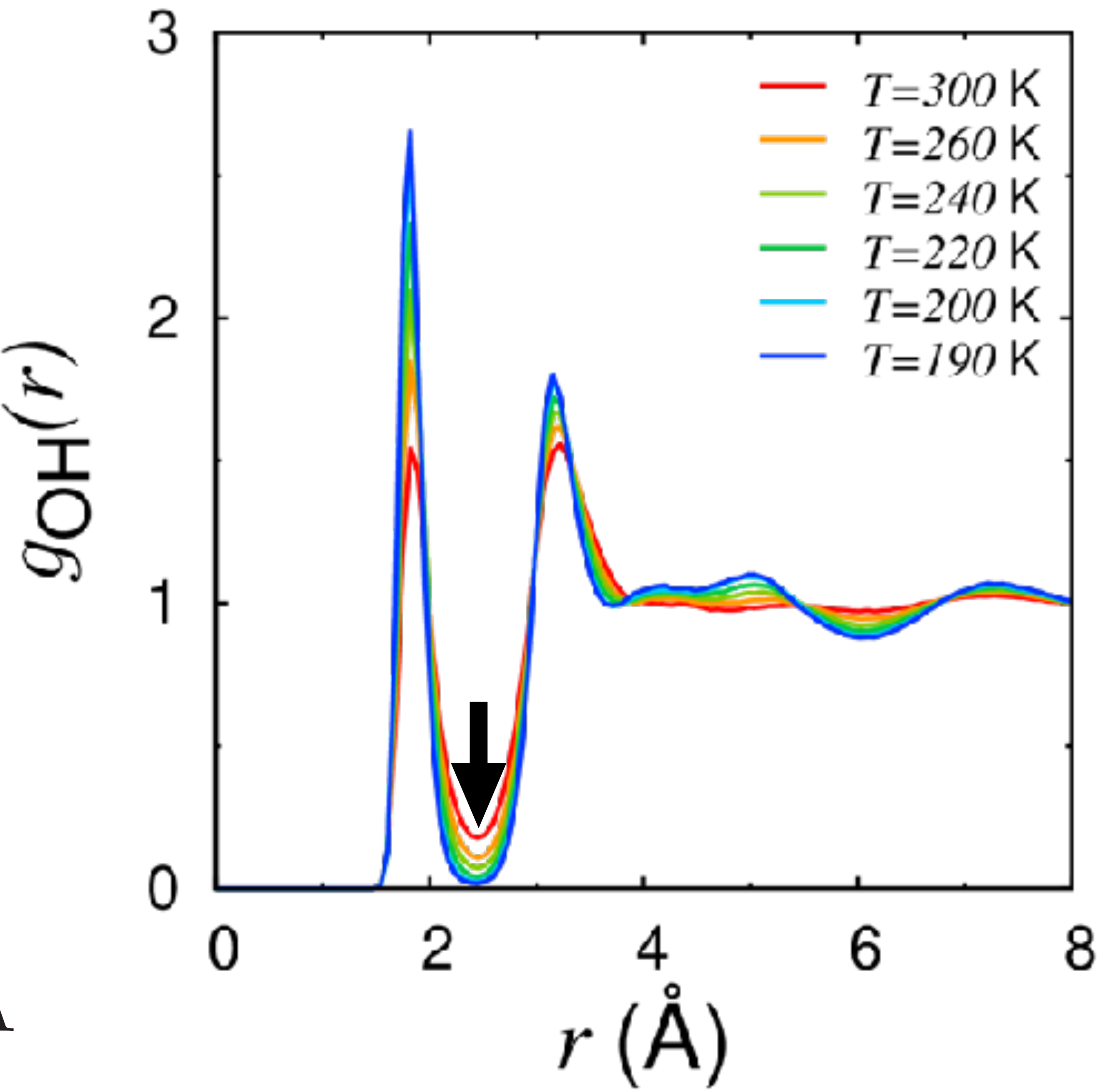
$D\tau_\alpha$ is a good indicator of $D\eta/T$

Hydrogen-bond breakages: rearrangements of local orders

wikipedia: Hydrogen bond



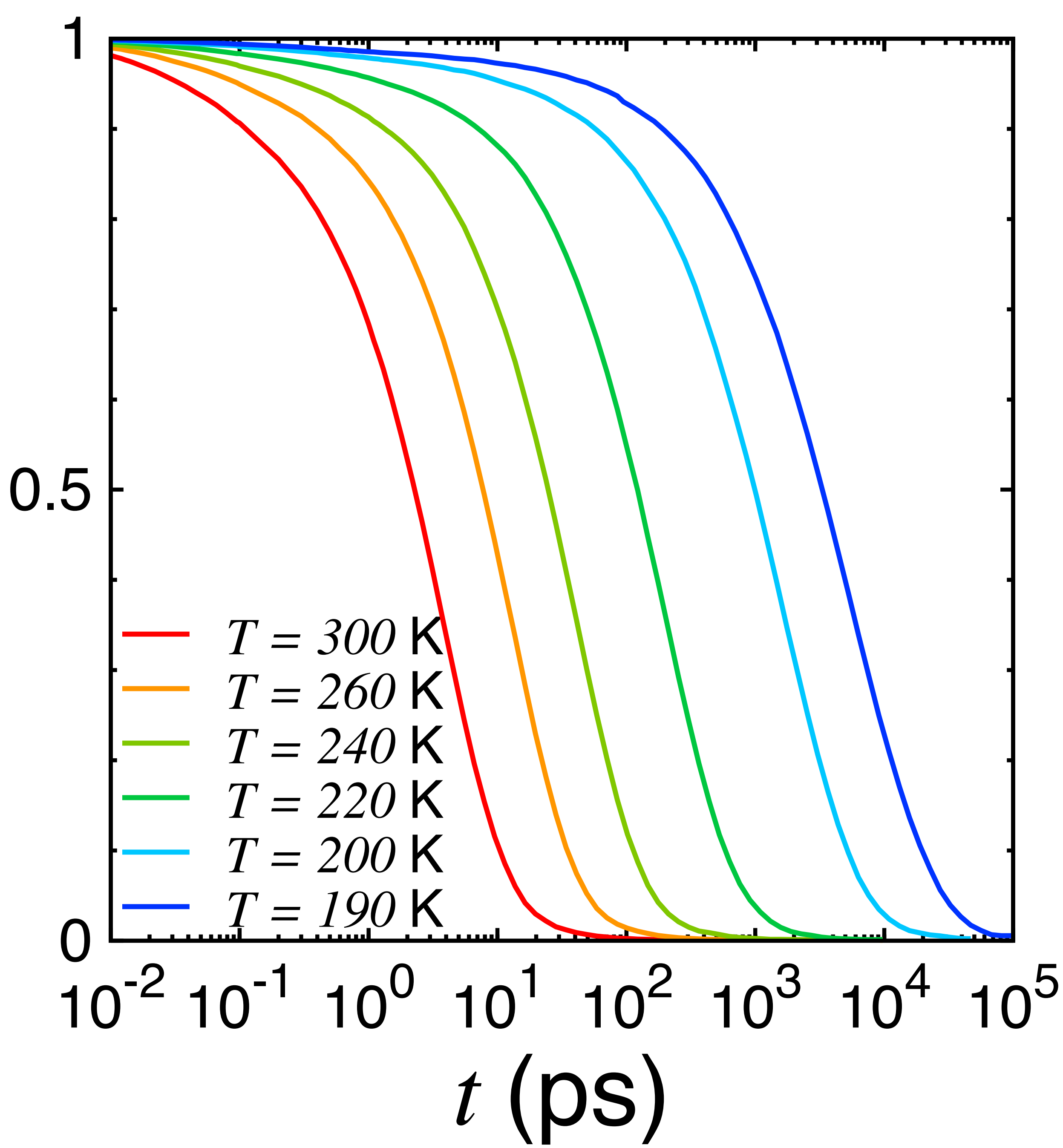
$r_{\mathrm{OH}} < 2.4$ Å



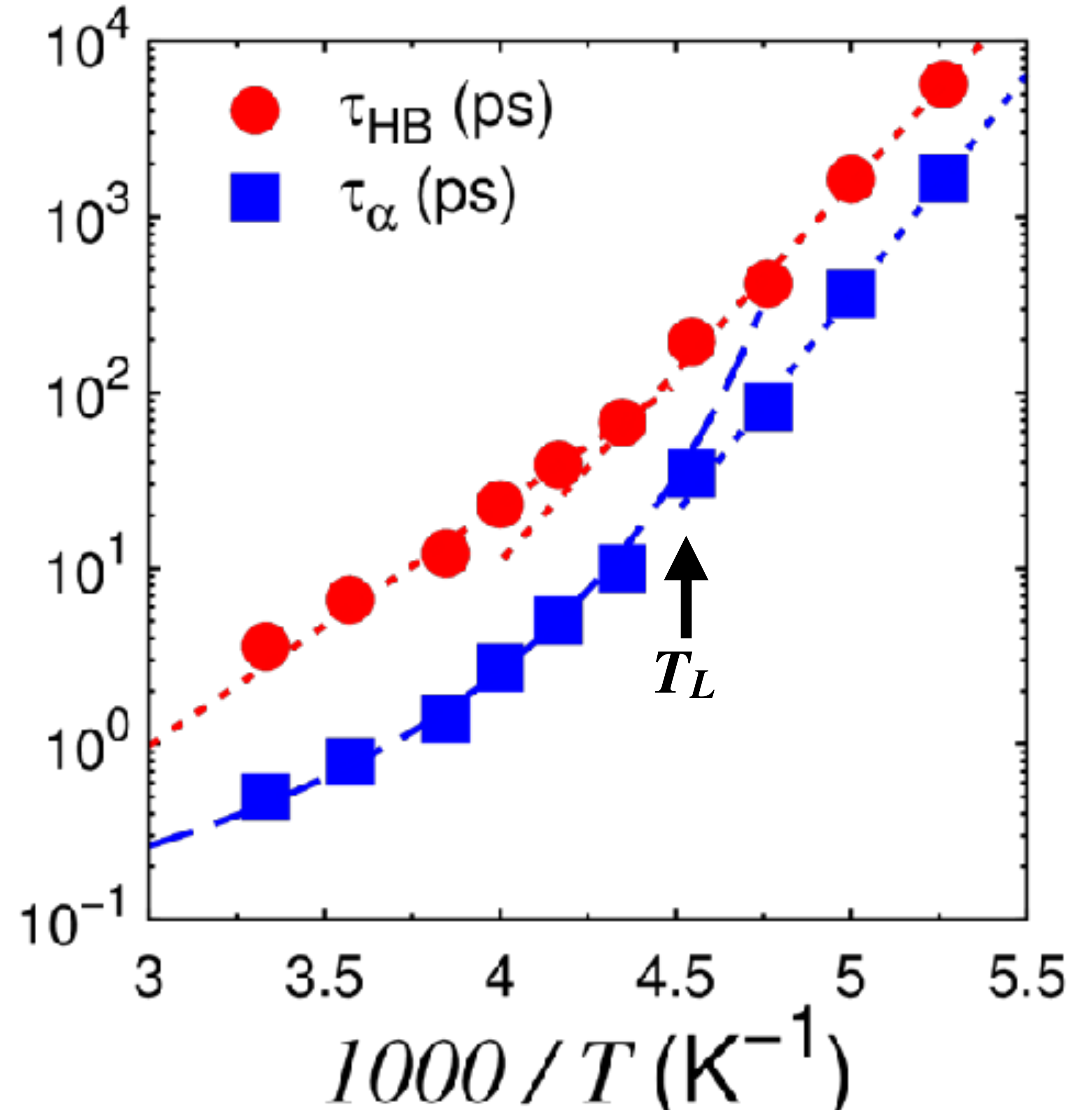
Quantifying the coordination number Z
⇒ applicable to other systems

Hydrogen-bond breakages: rearrangements of local orders

HB correlation

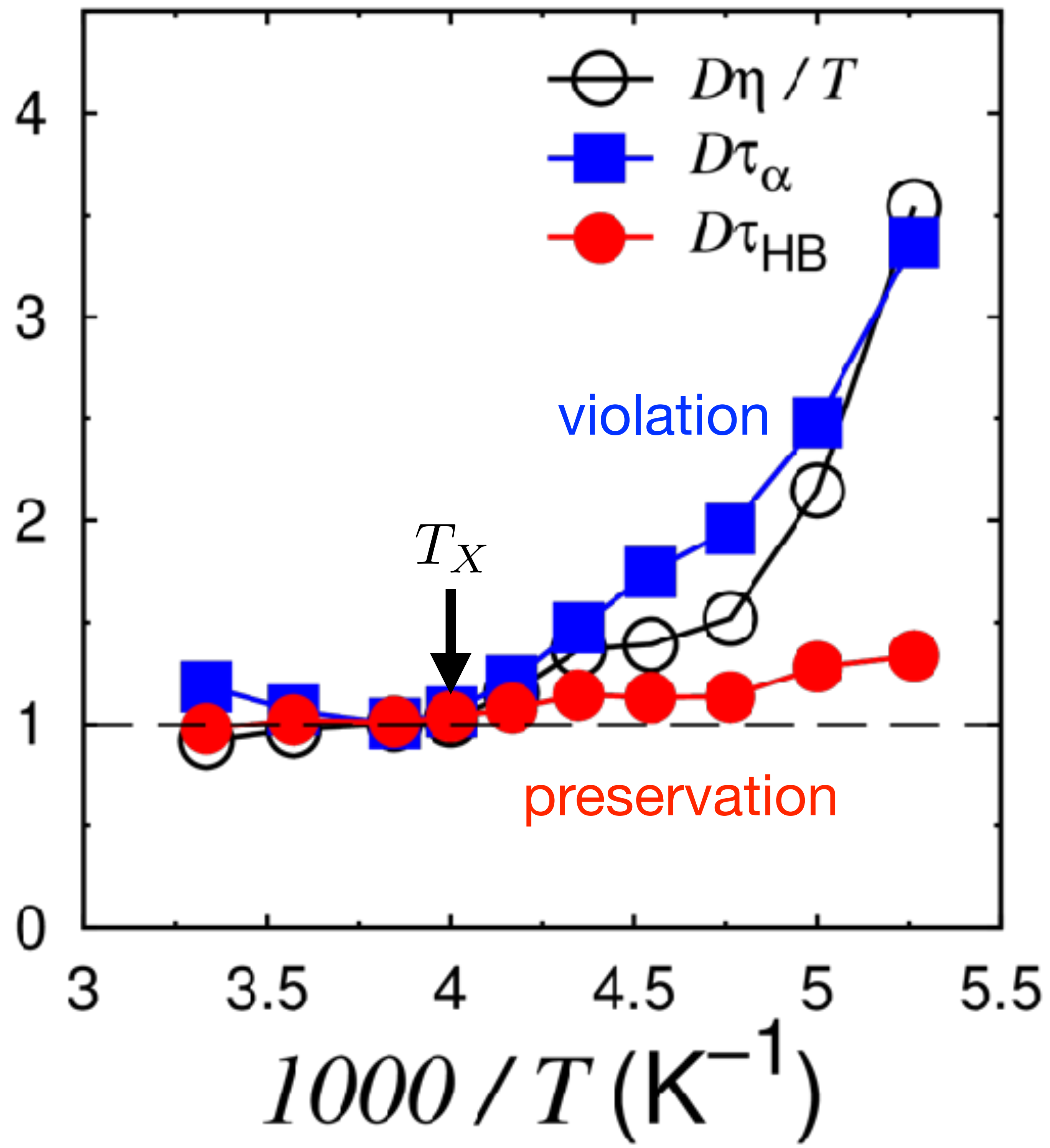


HB lifetime



No obvious fragile-strong crossover in τ_{HB}!!

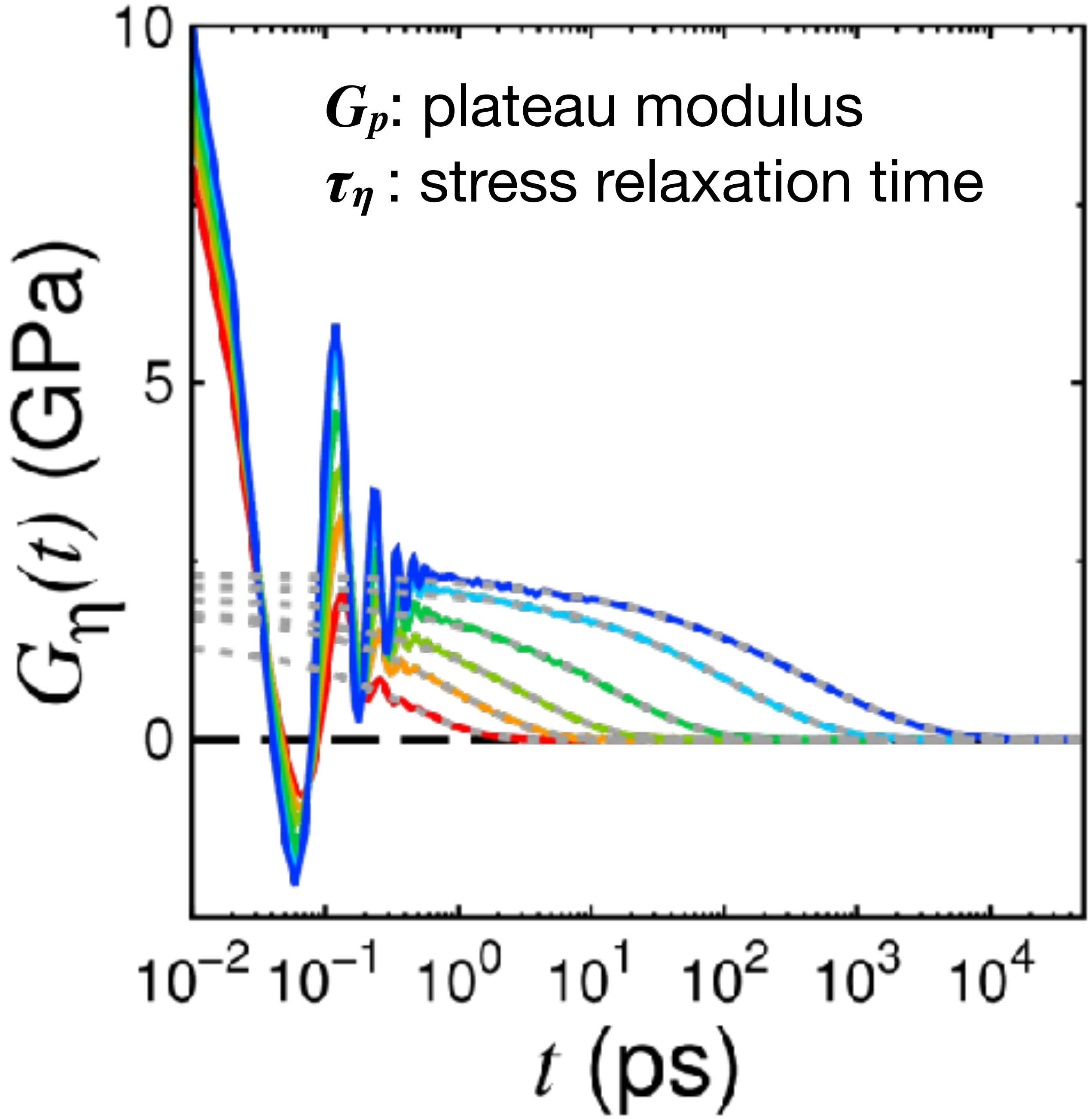
Violation/Preservation of SE relation



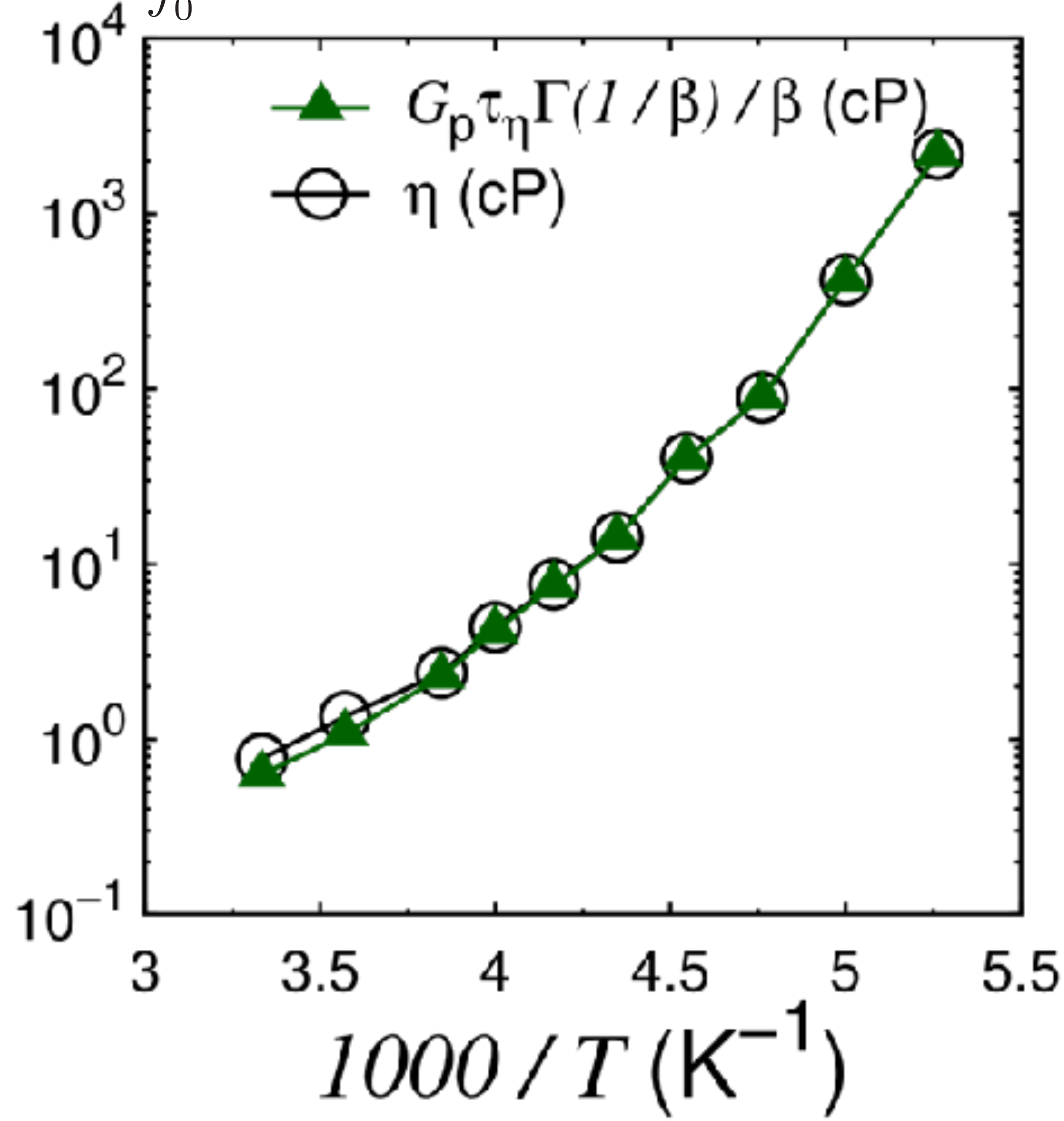
Coupling between diffusion ***D*** and HB lifetime ***τ_{HB}***

What is the relationship between time scales τ_{HB} and τ_α?

$$G_\eta(t) \simeq G_p \exp[-(t/\tau_\eta)^\beta]$$



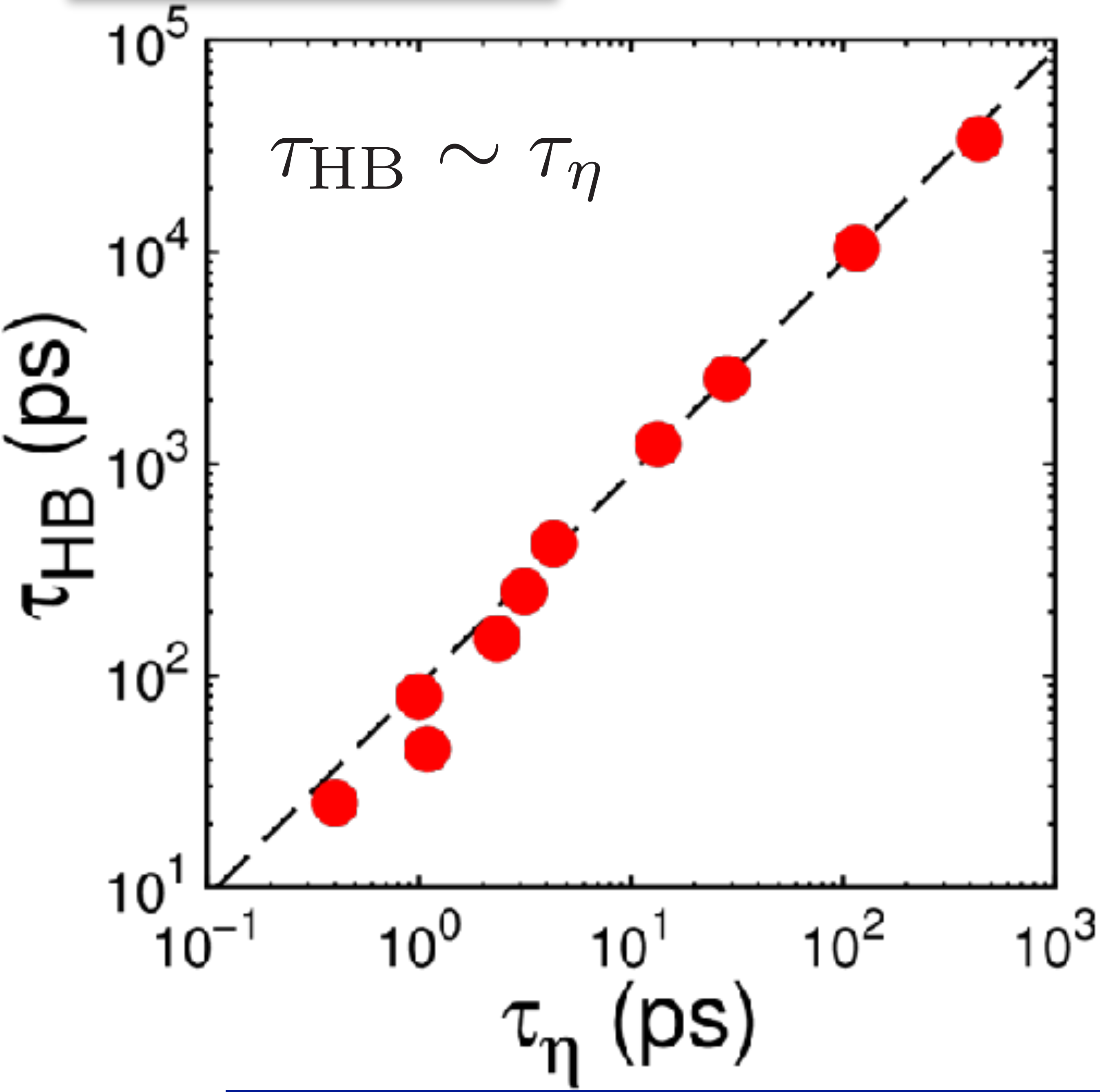
$$\int_0^\infty G_p \exp[-(t/\tau_\eta)^\beta]dt = G_p\tau_\eta\Gamma(1/\beta)/\beta$$



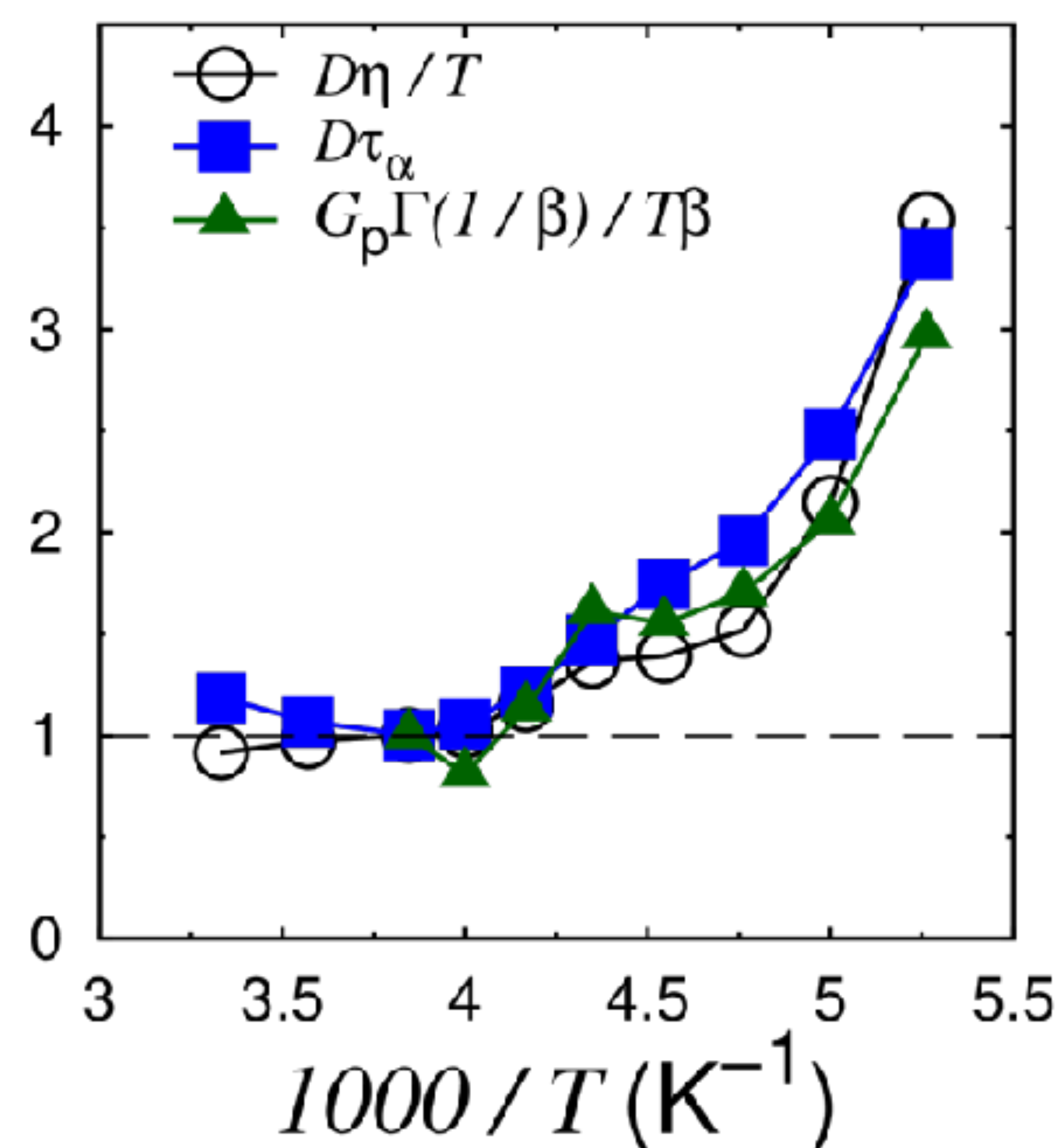
$\beta \approx 0.4$ (190 K): non-exponential stress relaxation!!

What is the relationship between time scales τ_{HB} and τ_α?

SE preservation



SE violation



$D\tau_{\rm HB} \sim D\tau_\eta$

$\eta = G_p \tau_\eta \Gamma(1/\beta)/\beta$

$D\eta/T \sim D\tau_\alpha \sim G_p\Gamma(1/\beta)/(T\beta)$

Summary:
Identifying time scales for violation/preservation of SE relation

diffusion constant D

Thermal activation jump motions determine this transport coefficient.
This is coupled with HB breakage lifetime τ_{HB}.

structural relaxation τ_α

The decoupling with D is related to not only non-Gaussianity in $F_s(k, t)$ but also non-exponentiality (β) and attaining solidity (G_p) in $G_\eta(t)$.

violation/preservation of SE relation

$$D\tau_{\mathrm{HB}} \sim D\tau_\eta$$

$$D\eta/T \sim D\tau_\alpha \sim G_p\Gamma(1/\beta)/(T\beta)$$

The mechanism of SE violation was fully clarified!!
Such classification is applicable to general glass-forming liquids including metallic alloys, silica glasses, ionic liquids, and so on.