Non-monotonic Relaxation Kinetics of Confined Systems

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Kinetics Models

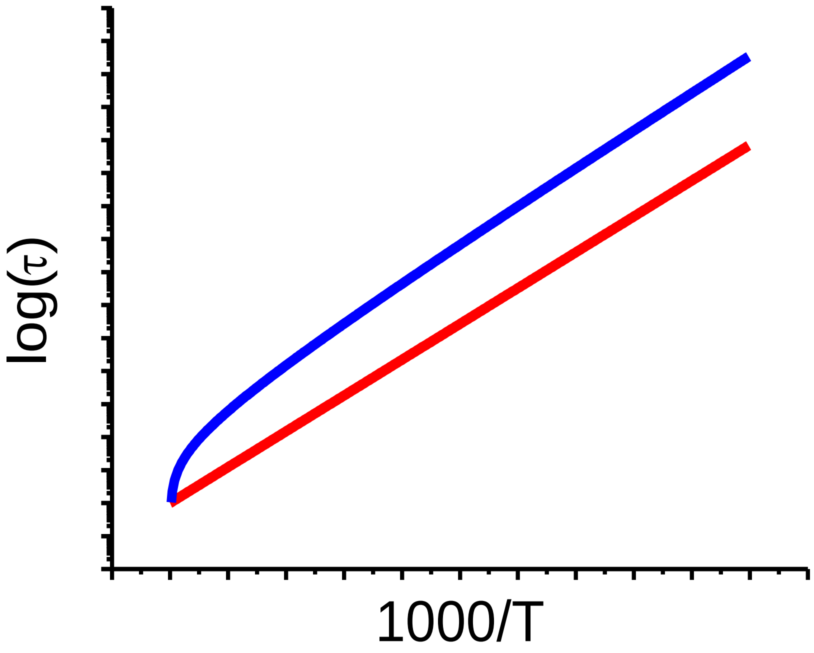
Transition state theory

Arrhenius Law (1889)

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$

Eyring Law (1935)

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta H}{kT} - \frac{\Delta S}{k}\right)$$



Kinetics Models

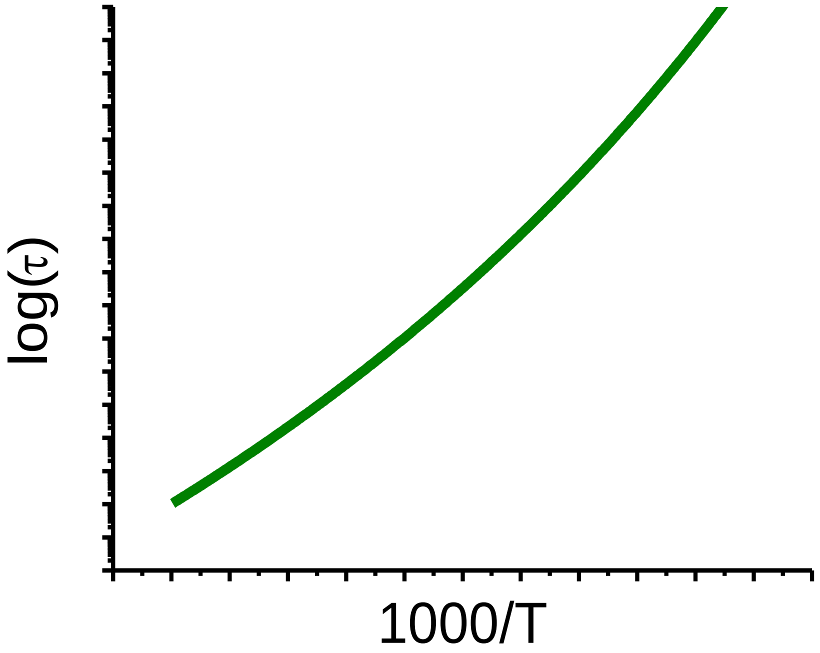
Free Volume concept

Vogel-Fulcher-Tamman
VFT (1921,1925,1926)

$$\tau = \tau_0 \exp\left(\frac{DT_k}{T - T_k}\right)$$

$$\tau = \tau_0 \exp\left(\frac{V_0}{V_F}\right)$$

$$V_F \sim T - T_k$$



Fox and Flory (1950)
Adam and Gibbs (1965)

Kinetics Models

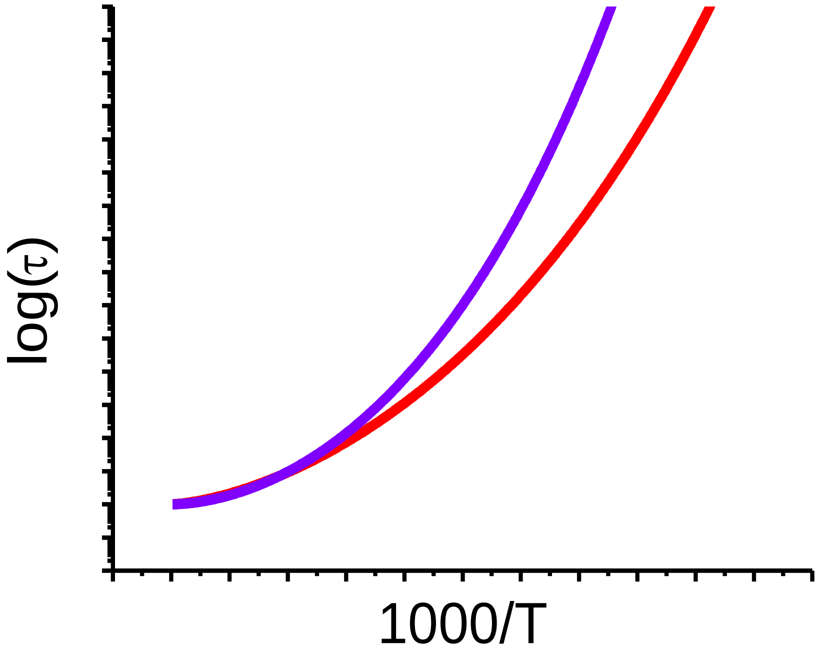
Bendler and Shlesinger (1987)
Mobile defects in amorphous state

$$\tau = \tau_0 \exp\left(\frac{B}{(T - T_K)^{3/2}}\right)$$

Bengtzelius, Götze and Sjölander (1984)
MCT

$$\tau = \tau_0 \exp\left(\frac{F}{(T - T_K)^{\gamma}}\right)$$

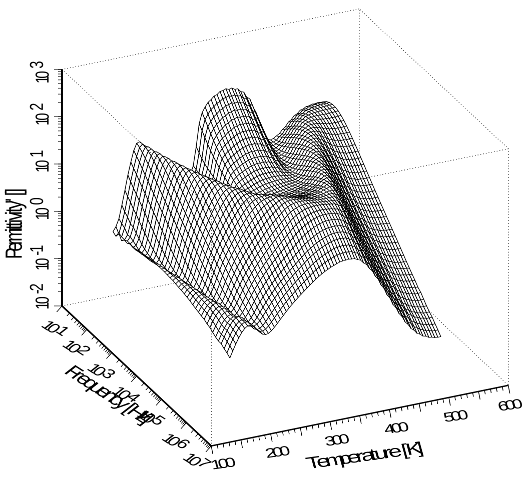
$\gamma \approx 1.76$

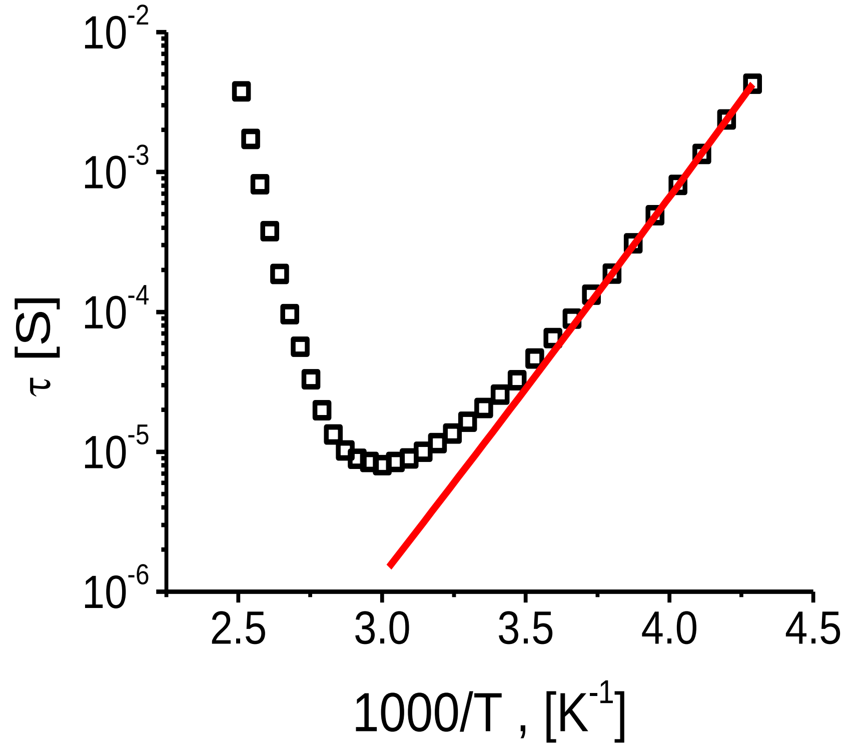


Non-monotonic Kinetics

Experimental observations

Water confined
in a porous glass sample
Gutina et al. (1998)





Non-monotonic Kinetics

The Model

$$\frac{1}{\tau} \sim p_1 p_2 \qquad p_1 = \exp\left(-\frac{E_a}{kT}\right) \qquad p_2 = \exp\left(-\frac{V_0}{V_F}\right)$$

Number of active particles

$$n = n_0 \exp\left(-\frac{E_b}{kT}\right)$$

Free Volume per particle

$$\frac{1}{V_F} \sim n_0 \exp\left(-\frac{E_b}{kT}\right)$$

Total volume of the system

$$V = const$$

$$\tau = \tau_0 \exp\left\{\frac{E_a}{kT} + \frac{V_0 n_0}{V} \exp\left(-\frac{E_b}{kT}\right)\right\}$$

Non-monotonic Kinetics

The Model

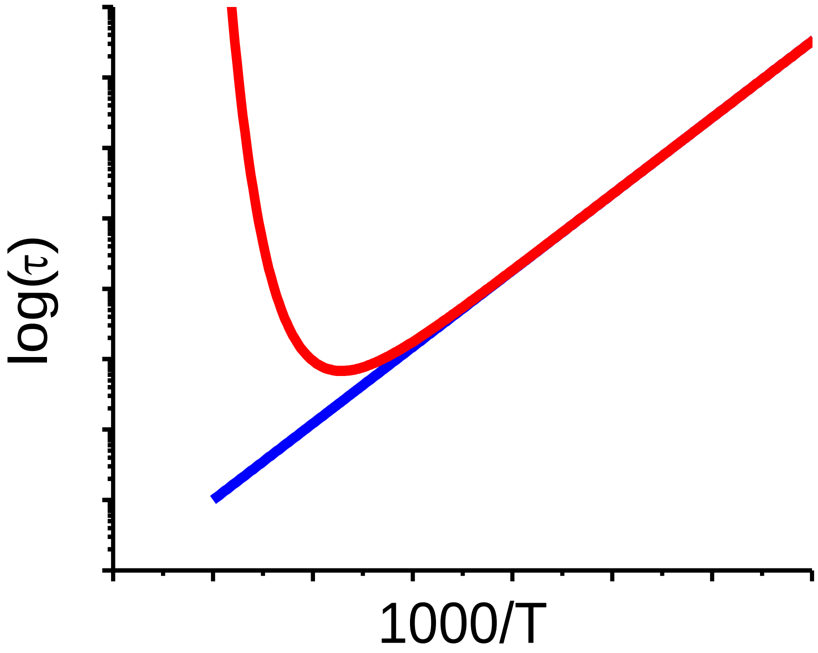
$$\tau = \tau_0 \exp\left\{\frac{E_a}{kT} + \frac{V_0 n_0}{V}\exp\left(-\frac{E_b}{kT}\right)\right\}$$

$$n_0 << \frac{V}{V_0}$$

Unconfined system with Arrhenius kinetics

$$n_0 >> \frac{V}{V_0}$$

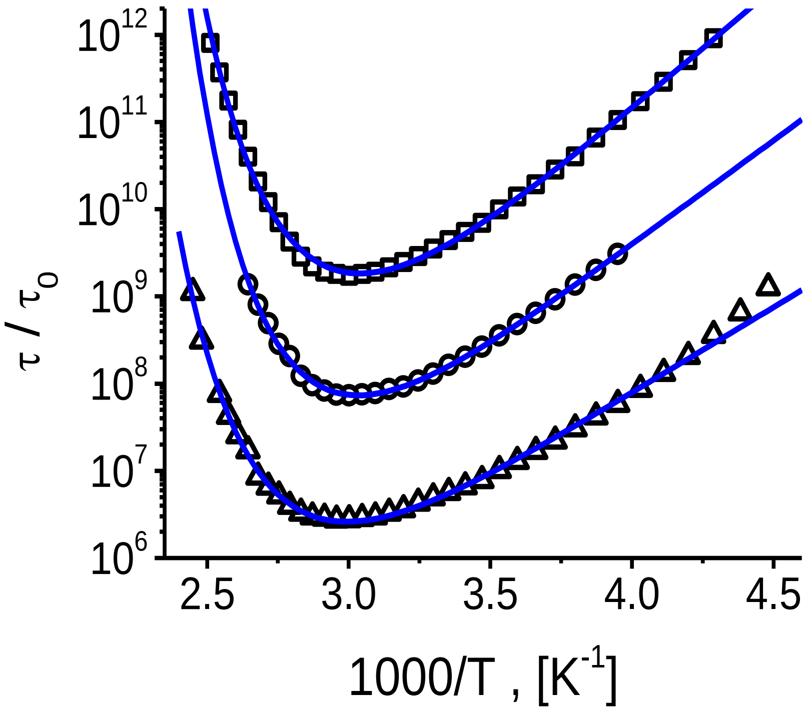
Confined system with non-monotonies kinetics



Model VS Experiment

Water confined in Porous Glasses

Sample	E_a [kJ/mol]	E_b [kJ/mol]	$n_0 V_0/V$	Ln τ_0
A ○	46	33	27×10^4	-27
B □	53	29	7×10^4	-33
C △	38	32	12×10^4	-26



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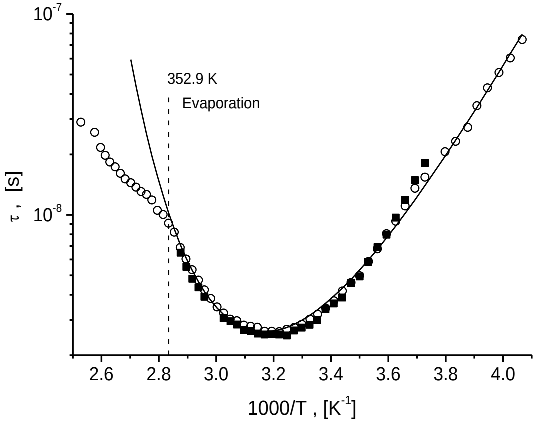
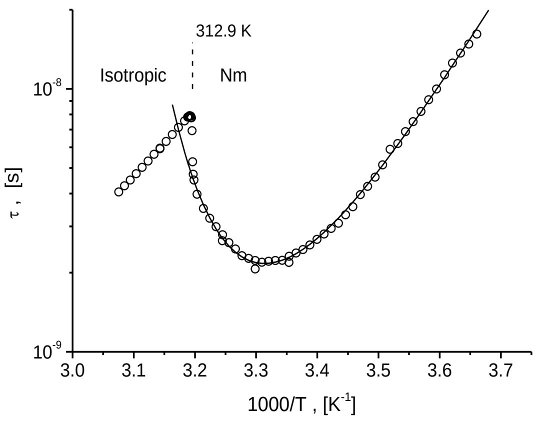
Model VS Experiment

Water in Zeolites



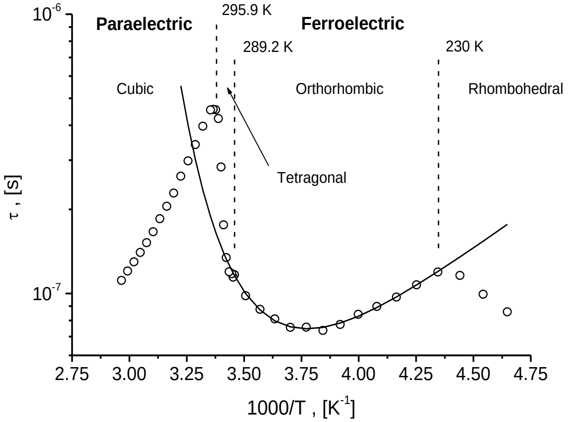
Schönhals et al. (2002)

Confined 8CB liquid crystal



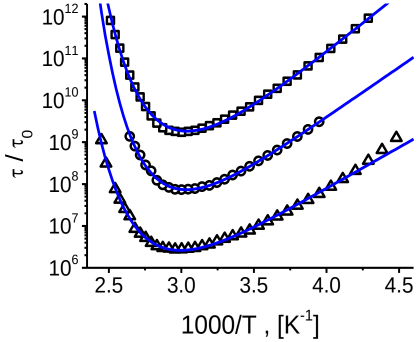
Aliev et al. (2002)

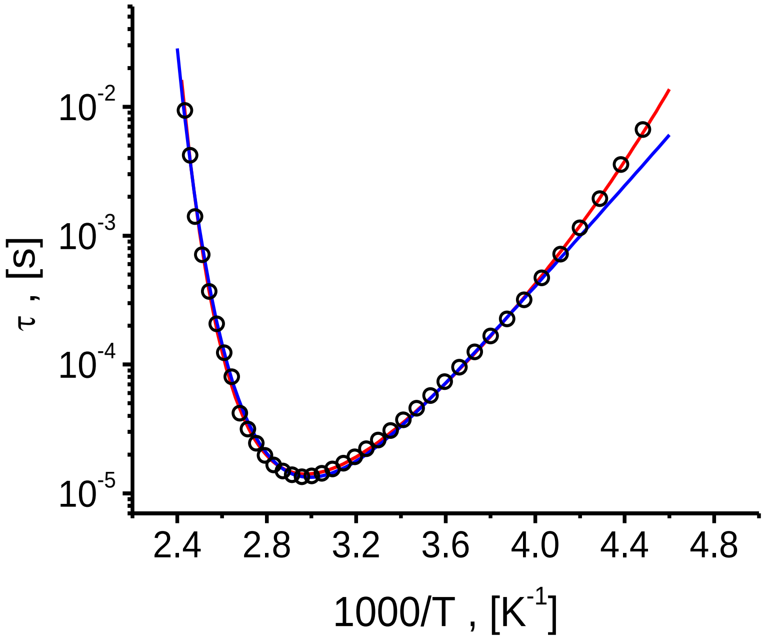
KTN ferroelectric crystal



Feldman et al. (2004, 2005)

Confined Supercooled Water



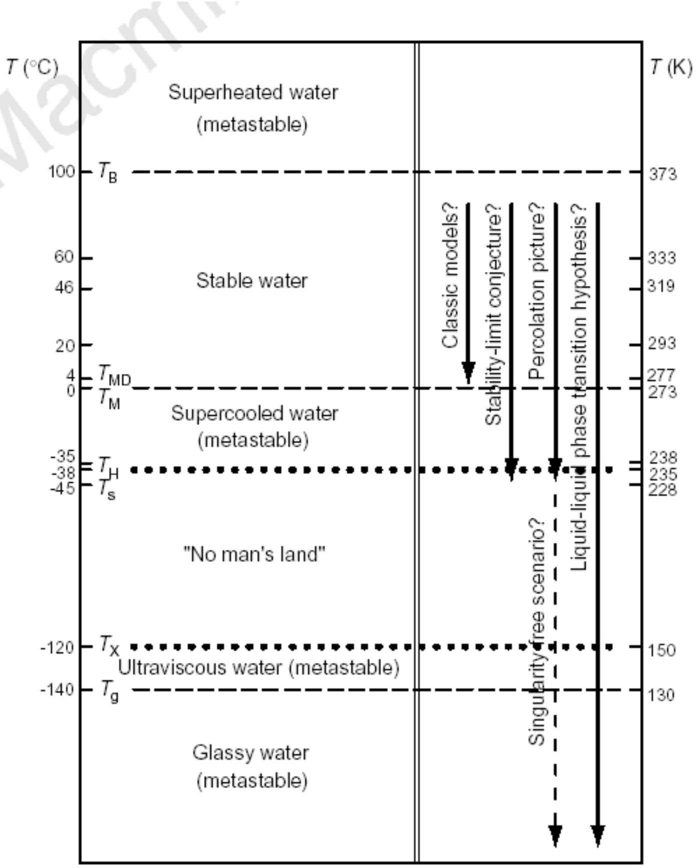


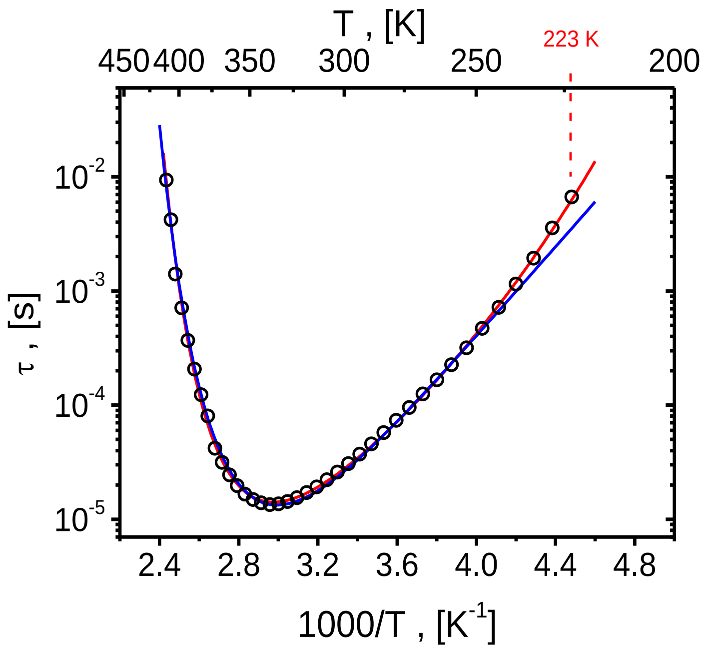
$$p_1 = \exp\left(-\frac{D\,T_k}{T - T_k} \right)$$

$$\tau = \tau_0 \exp\left\{ \frac{D\,T_k}{T - T_k} + \frac{V_0 n_0}{V} \exp\left(-\frac{E_b}{kT} \right) \right\}$$

Confined Supercooled Water

Mishima and Stanley (1998)





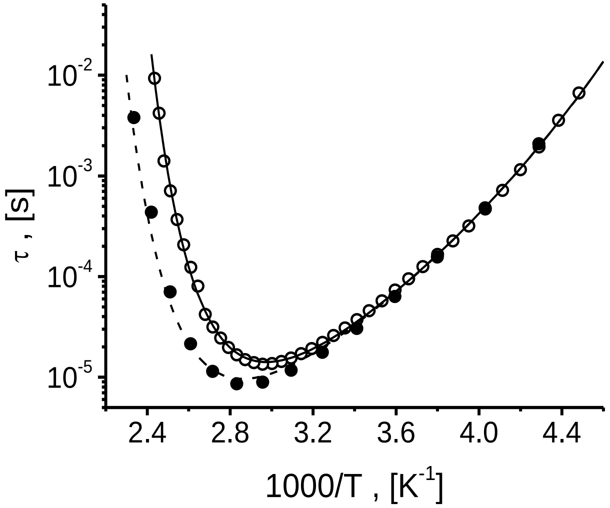
$$T_k = 124 \pm 7 \ [\text{K}] \qquad D = 10 \pm 2$$

$$T_g \sim 140 \ [\text{K}] \qquad D \sim 8$$

Johary et al. (1987), Smith and Kay (1999)

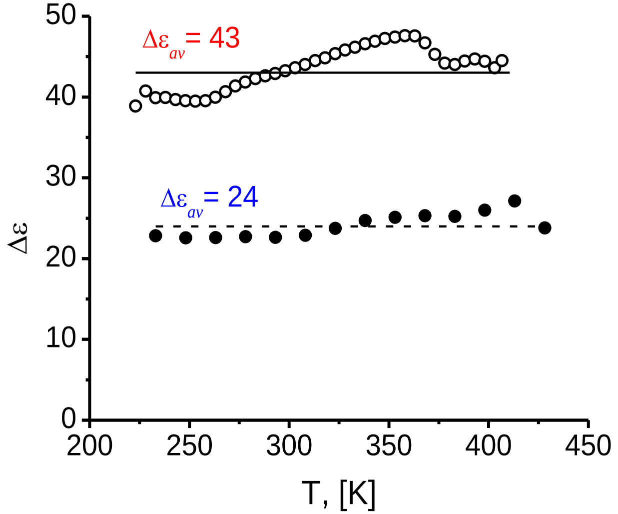
Confinement Factor

$$\tau = \tau_0 \exp\left\{ \frac{D\,T_k}{T - T_k} + \frac{V_0 n_0}{V} \exp\left(-\frac{E_b}{kT} \right) \right\}$$



$$\frac{V_0 n_0}{V}$$

$$n_0 \sim \Delta\varepsilon$$



$$\frac{\Delta\varepsilon_{av}}{\Delta\varepsilon_{av}} = 1.8$$

Protein folding kinetics
Random Energy Model

Derrida (1980)

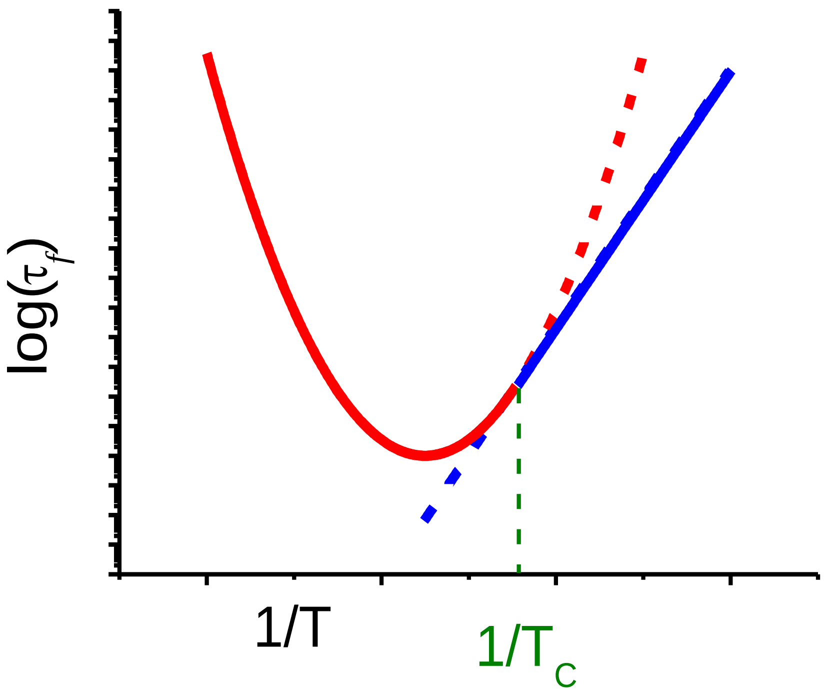
$$n(E) = \frac{\Omega}{\sqrt{2\pi\Sigma^2}} \exp\left(- \frac{(E - \overline{E})^2}{2\Sigma} \right)$$

Bryngelson and Wolynes (1987, 1989)

$$\ln\left(\frac{\tau_f}{\tau_0}\right) = \frac{E^*}{kT} + \frac{E_c T_c}{2k^2}\left(\frac{1}{T} - \frac{1}{T_c}\right)^2 \qquad T > T_c$$

$$\ln\left(\frac{\tau_f}{\tau_0}\right) = \frac{E^*}{kT} \qquad T < T_c$$

$$E_c = \overline{E} - \Sigma\sqrt{1 \ln \Omega}$$



Protein folding kinetics
Confinement in Conformation space

$$p_f = p_b^q p_n^{qN}$$

Probability to have an 'active' bond

$$p_b = \exp\left(-\frac{E_b}{kT}\right)$$

Probability to find an 'proper' connection

$$p_n = \exp\left(-\frac{\omega_0}{\omega_f}\right)$$

Total conformation volume

$$\Omega_0 = q^N$$

Free conformation volume

$$\omega_f = \frac{\Omega_0}{N_d}$$

$$\omega_0 = \frac{\Omega_0}{qN}$$

$$\omega_f = qN\exp\left(\frac{E_b}{kT}\right)$$

$$\tau_f \sim \frac{1}{p_f} \sim q\frac{E_b}{kT} + qN\exp\left(-\frac{E_b}{kT}\right)$$

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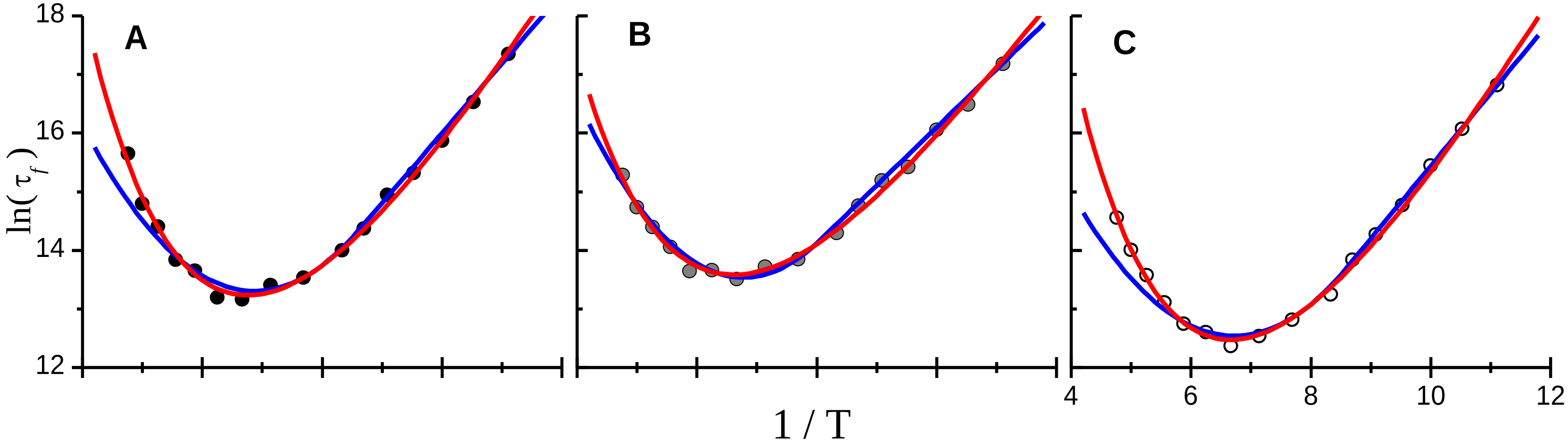
Protein folding kinetics

Models VS simulation data

Simulation data from Shaknowich et al. 1998



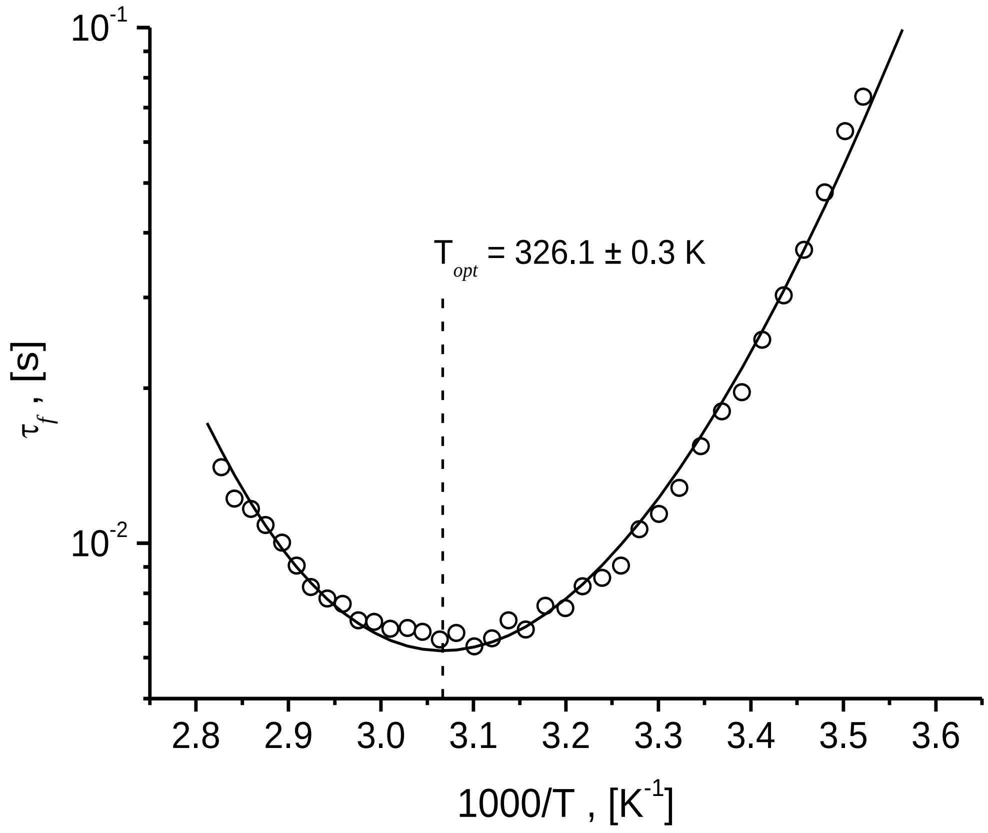
$N = 27$

	REM					Confinement Model			
	$\ln \tau_0$	E_c	E^*	$1/T_C$	χ^2	$\ln \tau_0$	E_b	q	χ^2
A	4.20	-5.92	1.19	8.60	0.077	-1.18	0.49	3.26	0.010
B	6.10	-6.32	0.99	58.04	0.016	1.84	0.50	2.73	0.008
C	3.04	-5.68	1.24	8.60	0.083	2.14	0.49	3.40	0.006

Protein folding kinetics

Model VS experimental data

Data from Fersht et al. 1996 (CI2)



$\ln \tau_0 = -83$

$E_b = 11.3$

$qN = 967$

More experimental data needed

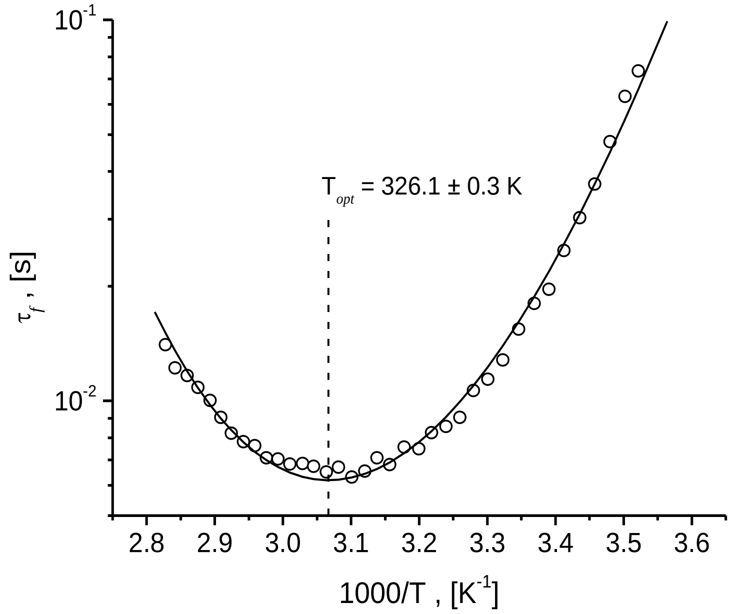
Protein folding kinetics

Levintahal's Paradox (1969)

$$\tau_f = \tau_0 q^N$$

Algebraic scaling

$$\tau_{fast} = \tau_0 (eN)^q$$



$$q \sim 2 \div 3$$

Camacho and Thirumalai (1993)

Have To be tested

$$T_{opt} = \frac{E_b}{k \ln N}$$

Conclusions

- **Non monotonous kinetics can be a result of confinement either in real or in conformational space**

✓ **Confined water can be supercooled below its homogeneous nucleation point which opens new possibilities for investigation of water glass state**

✓ **The concept of confinement in conformational space can serve as a paradigm for protein folding kinetics, which leads to known algebraic scaling for protein folding times.**

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