The Temperature Dependence of the Relaxation Time in ultraviscous liquids

Is there evidence for a dynamic divergence in data?

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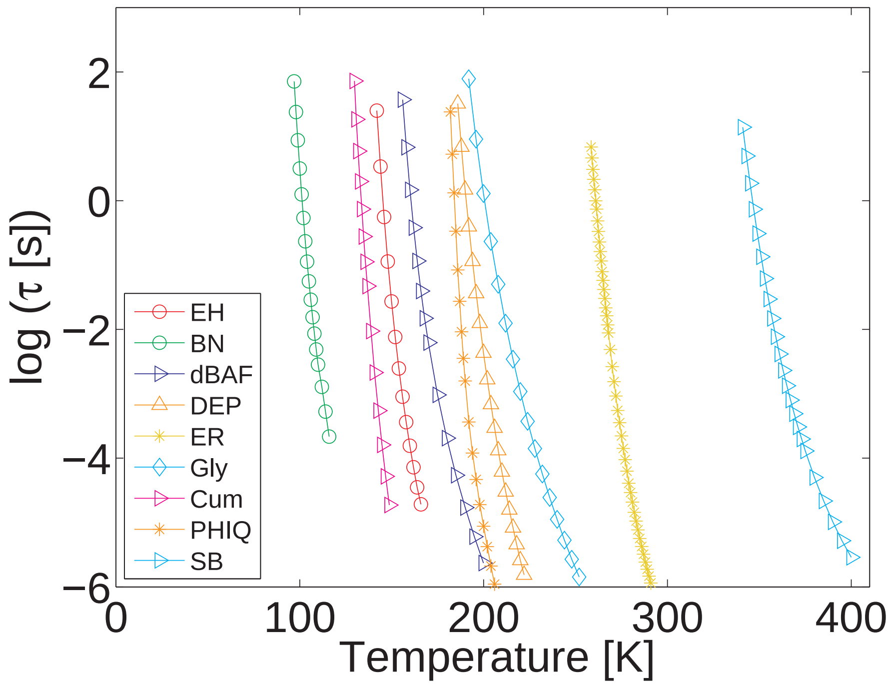
Fragility



2
0
−2
−4
−6
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100
200
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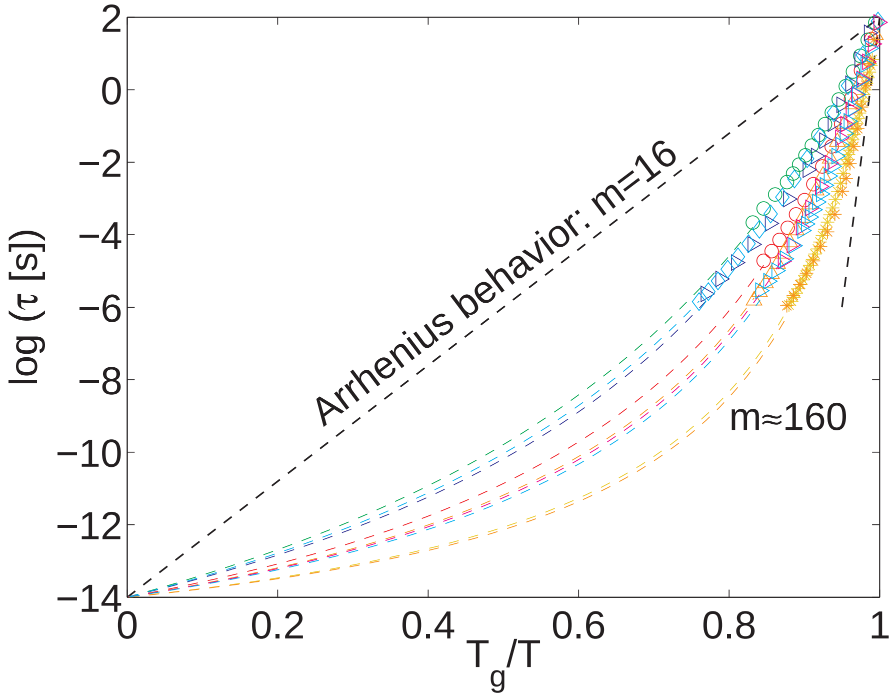
log (τ [s])
Temperature [K]
EH
BN
dBAF
DEP
ER
Gly
Cum
PHIQ
SB

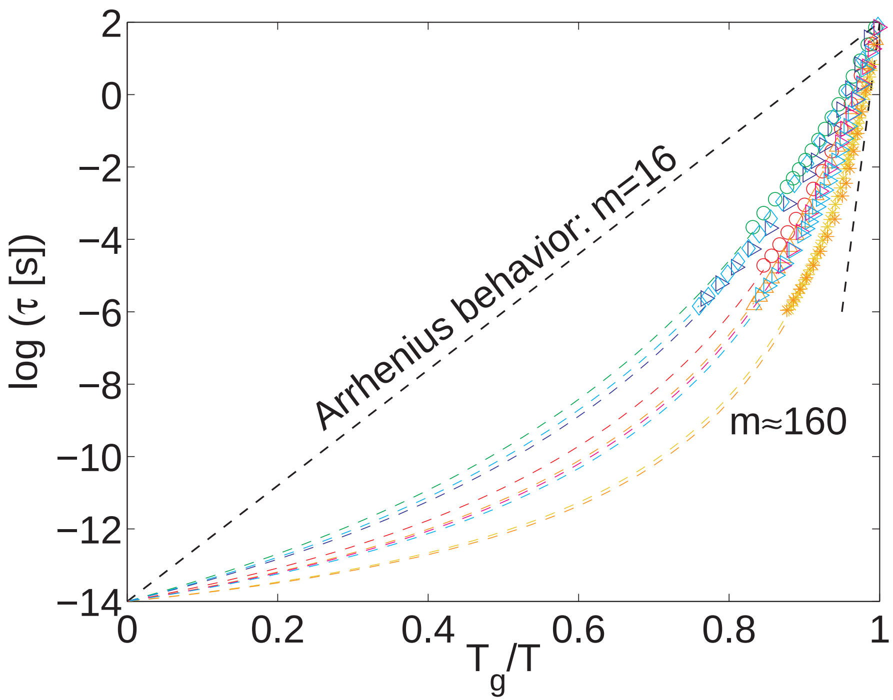
Fragility



Arrhenius equation:

$$\tau = \tau_0 \times \exp\left(\frac{\Delta E}{k_B T}\right)$$

Fragility



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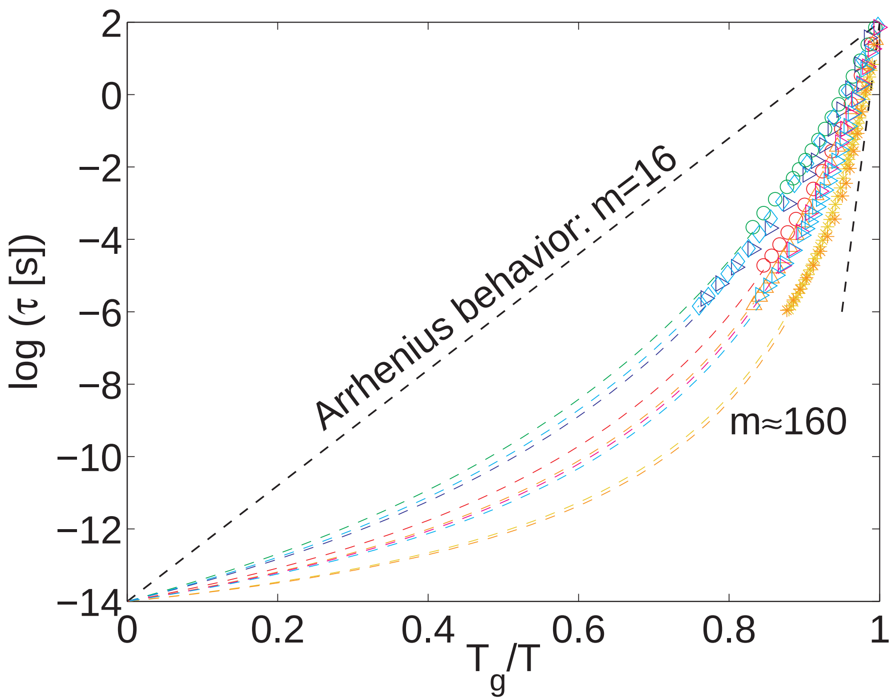

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Fragility index: $m \equiv \left.\frac{d\log\tau}{d(T_g/T)}\right|_{T_g}$

Empirical equations

- VFT equation [H. Vogel (1921), G. S. Fulcher (1925), G. Tammann, (1925)]:

$$\tau = \tau_0 \exp\left(\frac{A}{T - T_0}\right) \quad \Rightarrow \quad \Delta E(T) \propto \frac{T}{T - T_0},\ T_0 < T_g$$

- Avramov equation [G. Harrison (1976), I. Avramov (2005)]:

$$\tau = \tau_0 \exp\left(\frac{B}{T^n}\right) \quad \Rightarrow \quad \Delta E(T) \propto T^{-n+1},\ n \geq 1$$

Theoretical models

’Derivations’ of the VFT-equation:

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V. Lubchenko & P.G. Wolynes, Annu. Rev. Phys. Chem., 58, p. 235-266 (2007)

Theoretical models

Entropy-model: $$\Delta E \propto \frac{1}{S_c(T)}$$

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[Cohen & Turnbull (1959)]

Theoretical models

GLASS AND TIME

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Shoving-model: $\Delta E \propto G_\infty$

[Dyre, Christensen, & Olsen (1996)]

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Other elastic models E [Eyring (1936), Dyre (2006)]

How do we test the existence of a finite T_0?

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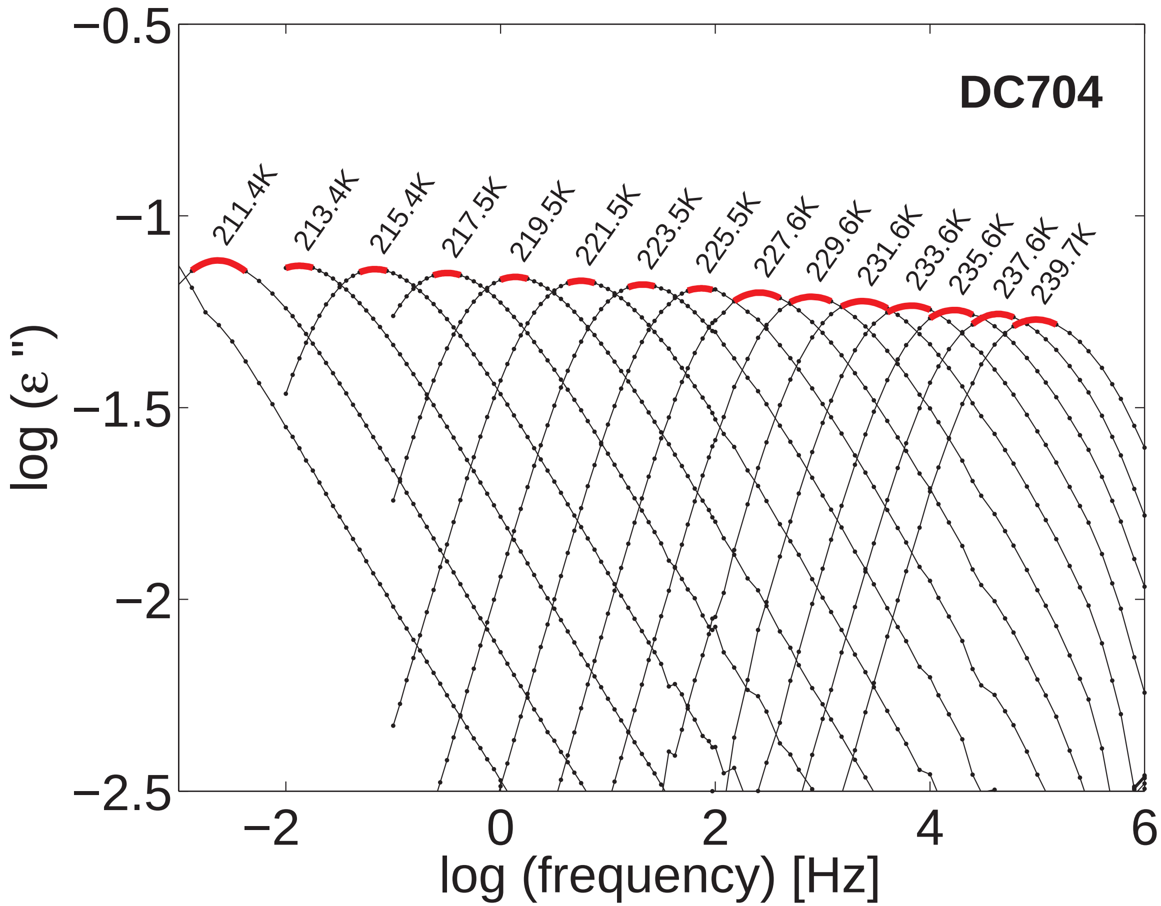
A dynamic divergence is probable

$$\Updownarrow$$

the VFT-equation fits data better than other fitting functions
with the same number of parameters

Data used in the analysis

Dielectric data: the most precise and most abundant data



$$\tau := \frac{1}{f_p}$$

Data used in the analysis

Dielectric data: the most precise and most abundant data

Requirements:

- dynamical range $[10^{-6} : 10^{3}]$s
- spanning at least 4 decades in relaxation time
- at least 5 temperatures measured
- no monoalcohols, polymers, or plastic crystals

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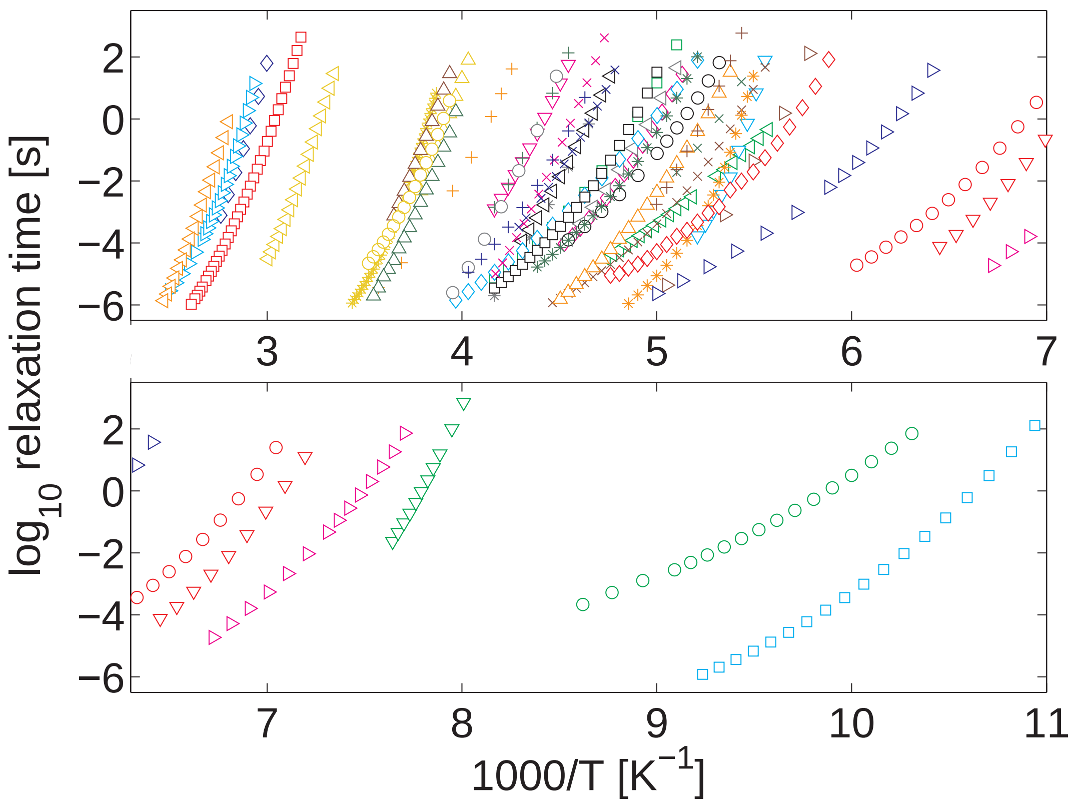

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42 ultraviscous organic liquids

Examples of fits

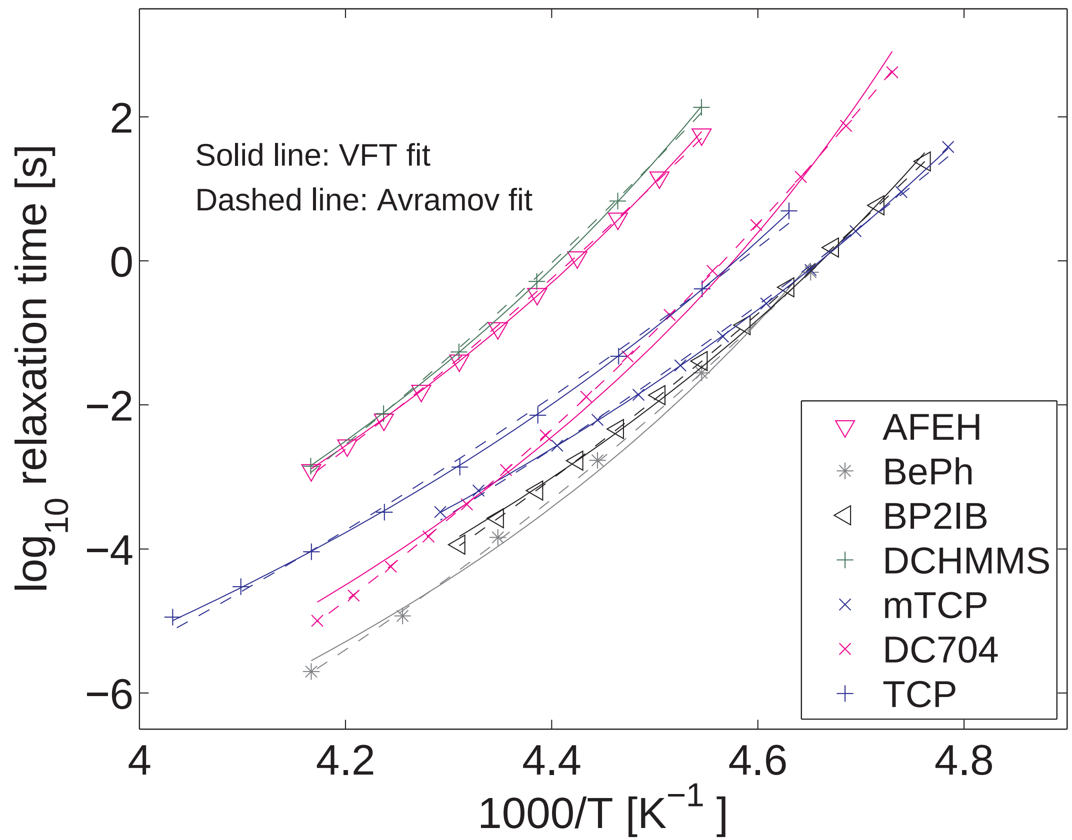
Both equations have 2 parameters (prefactor fixed: $\tau_0 = 10^{-14} s$)

VFT equation (solid line):

$$\tau = \tau_0 \exp\left(\frac{A}{T - T_0}\right)$$

Avramov equation (dashed line):

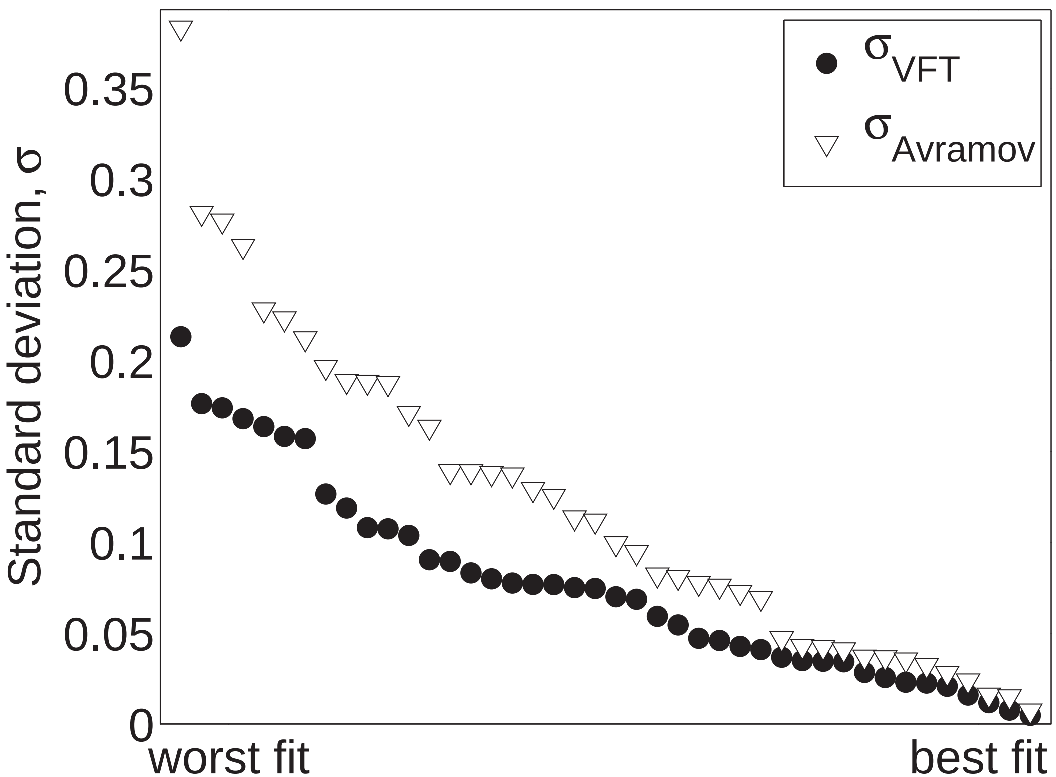
$$\tau = \tau_0 \exp\left(\frac{B}{T^n}\right)$$



Both fit data really nicely - but is one better than the other?

'Goodness' of the fits

Variance: $$\sigma^2 = \frac{1}{N-n}\sum_{i=1}^{N}\left(\log_{10}\tau_i^{\text{data}} - \log_{10}\tau_i^{\text{model}}\right)^2$$



$$\overline{\sigma}_{\text{VFT}} = 0.077$$

$$\overline{\sigma}_{\text{Avramov}} = 0.12$$

... the VFT equation on average fits better than the Avramov equation!

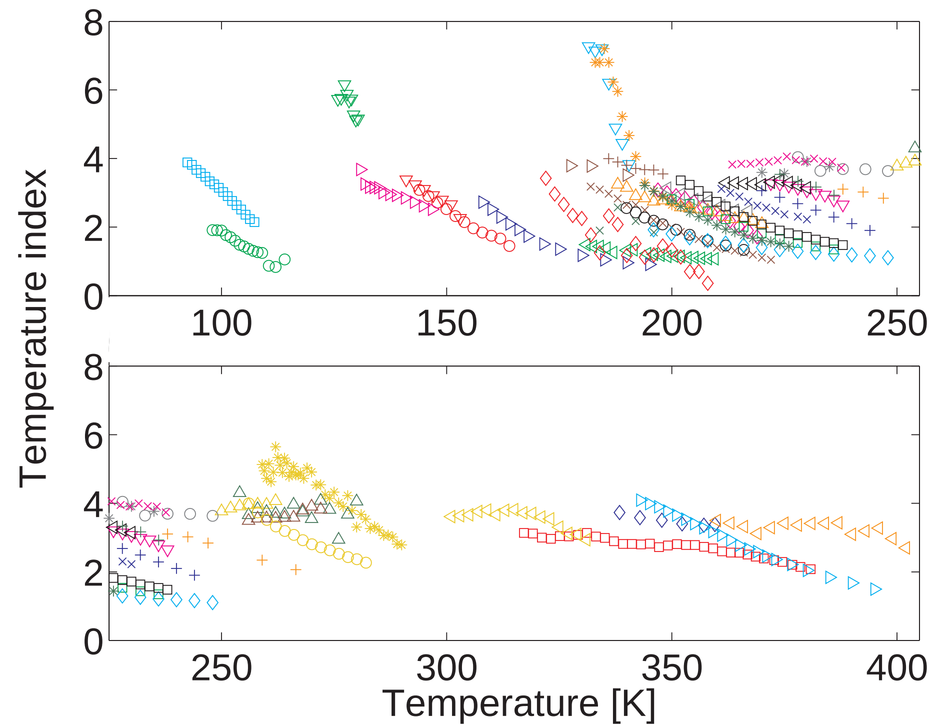
Temperature index

Definition [Dyre & Olsen, 2004]:

$$I_{\Delta E} \equiv -\frac{d\ln \Delta E}{d\ln T}$$

Connection to fragility:

$$m = 16(I_{\Delta E}(T_g) + 1)$$



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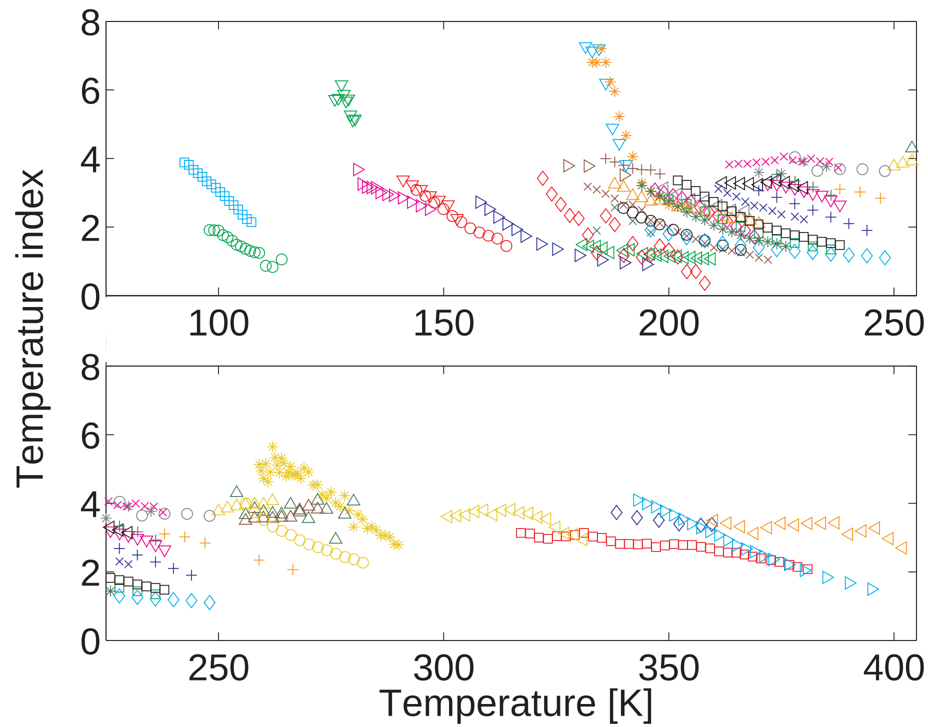

Calculated for models: $I^{\text{VFT}} = \frac{T_0}{T - T_0}, \quad I^{\text{Av.}} = n - 1$

Functions without divergence

FF1: $I = 1 - T_1/T$, FF2: $I = (T_2/T)^2$

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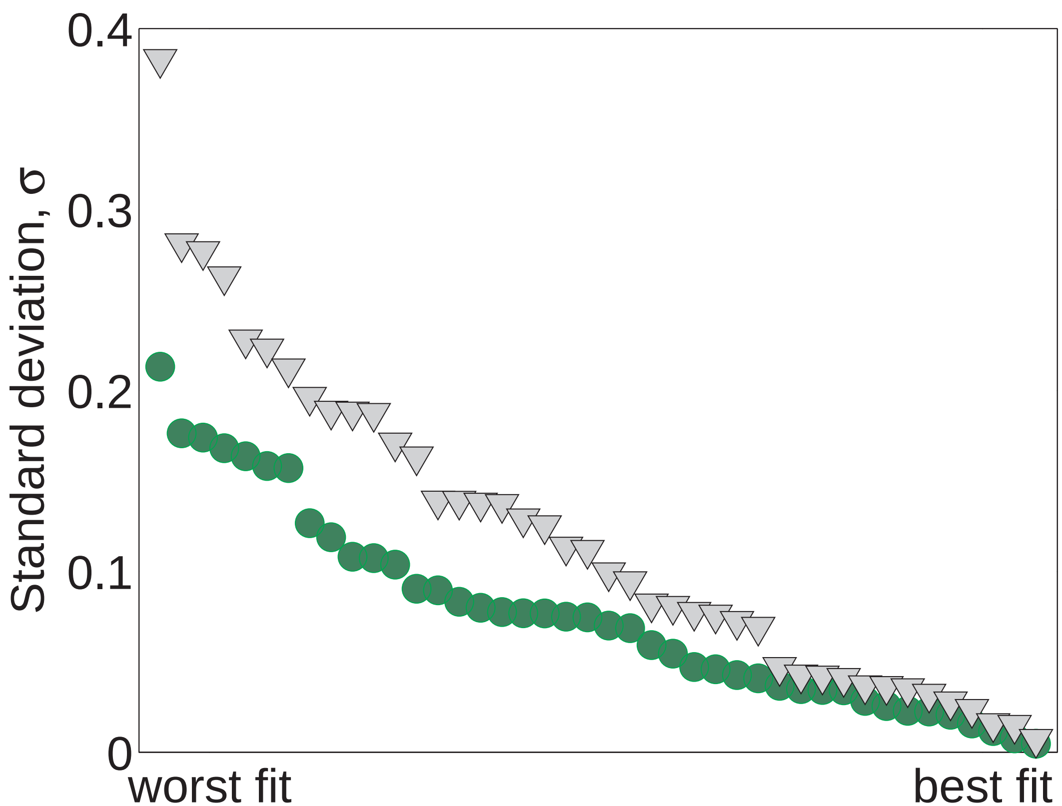
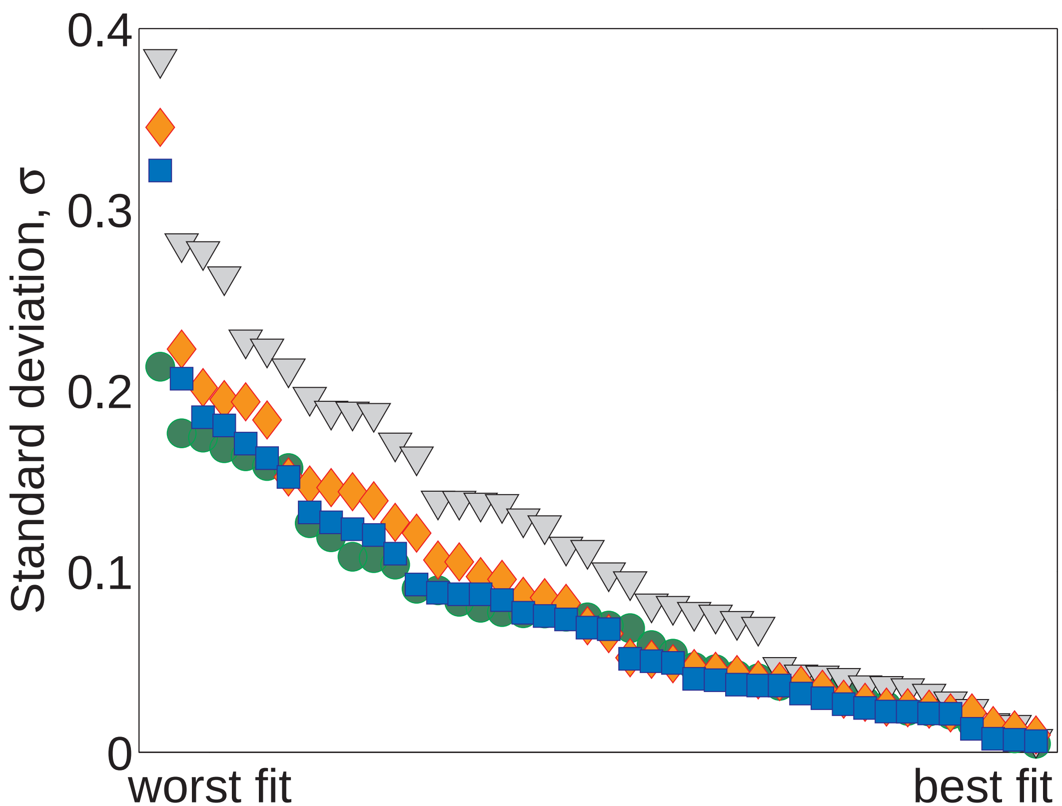


Avramov: $\Delta E \propto T^{-n+1}$

VFT: $\Delta E \propto T/(T-T_0)$

Functions without divergence

FF1: $I = 1 - T_1/T$, FF2: $I = (T_2/T)^2$



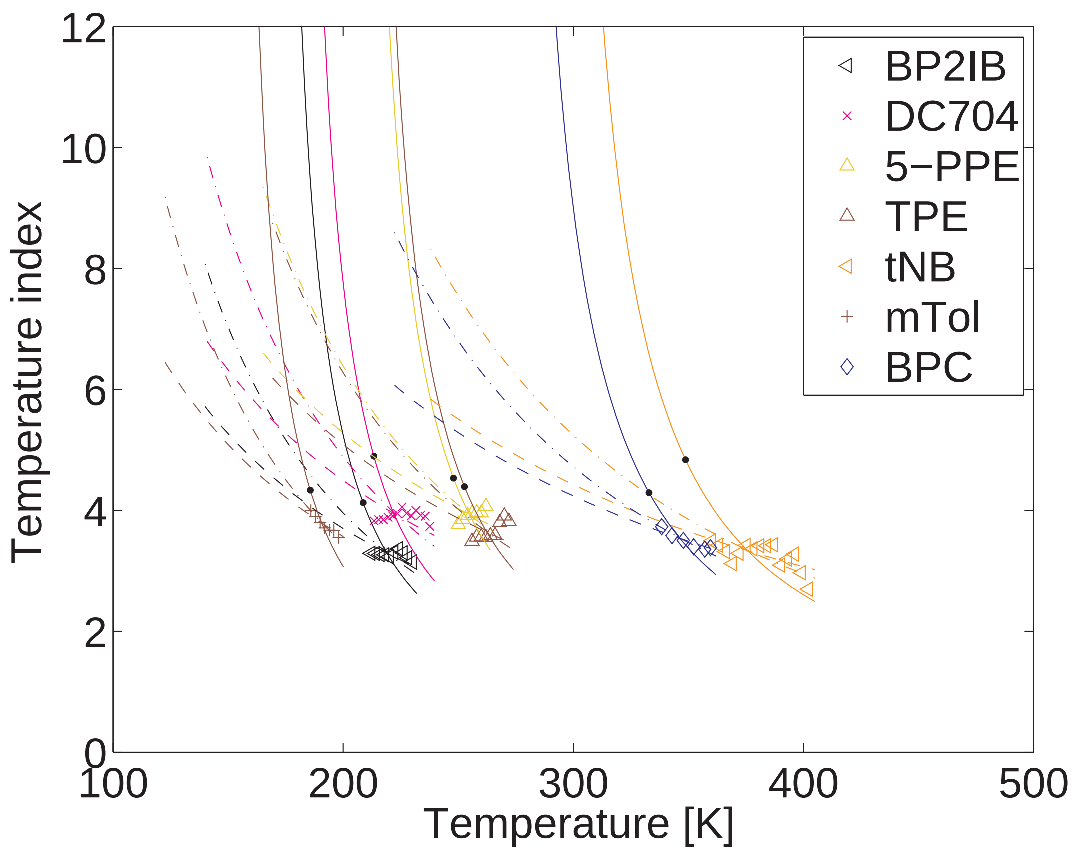
Avramov: $\Delta E \propto T^{-n+1}$

VFT: $\Delta E \propto T/(T - T_0)$

FF1: $\Delta E \propto T \exp\left(\frac{T_1}{T}\right)$

FF2: $\Delta E \propto \exp\left(\frac{T_2^2}{2T^2}\right)$

Index and model predictions



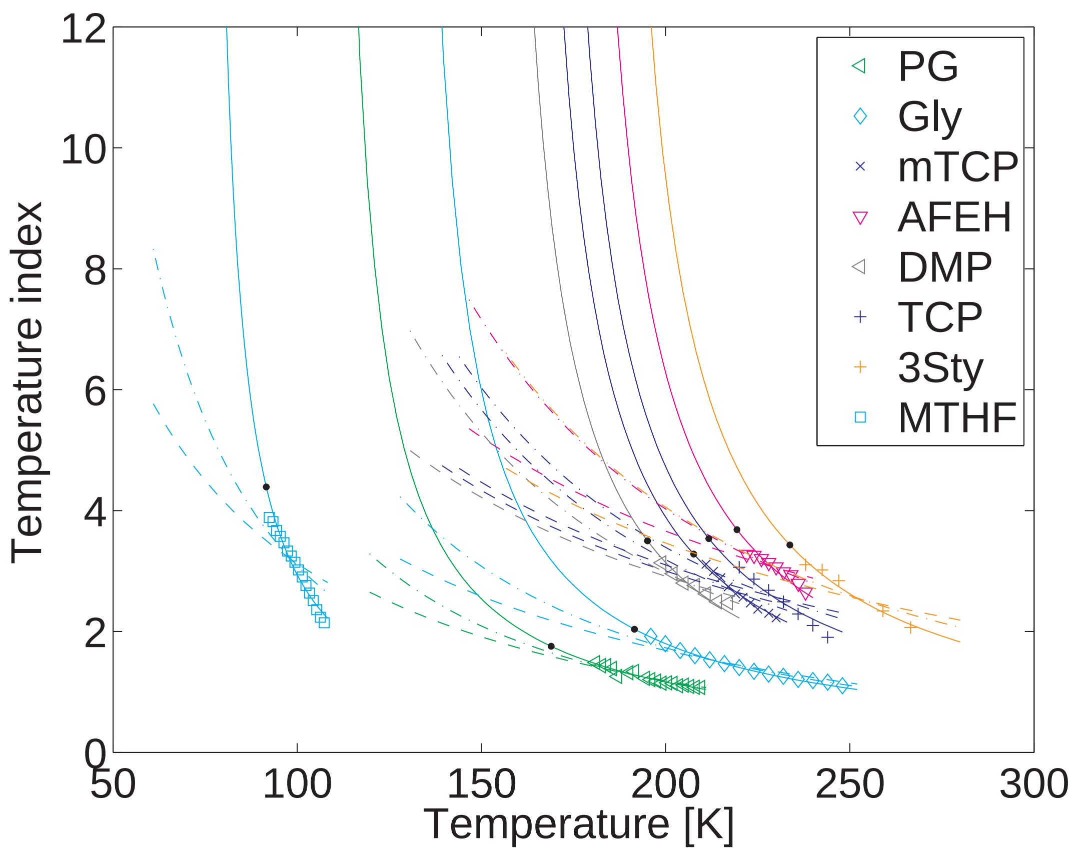
VFT: full line

FF1: Dashed line

FF2: Dash-dotted line

(Avramov: constant)

Index and model predictions



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Summary

- the VFT equation on average fits better than the Avramov equation (with a fixed τ_0)
- the temperature index of the activation energy is itself temperature dependent
- little evidence in the data for a dynamic divergence

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Thank you for your attention!