Density temperature scaling of fragility in a model glass-former

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Density-temperature scaling of the fragility in a model glass-former

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Acknowledgement

- We thank CCMS, JNCASR for computational facility.

What is the question ?

If density temperature scaling holds, then is kinetic fragility independent of density ?

Why is this question interesting ?

❖Concept of fragility useful as a organizing principle to rationalize huge amount of data in many different liquids over a large range of temperature and relaxation time.

❖By definition, kinetic fragility is independent of temperature but could be a function of density (pressure). **Further simplification** of liquid properties will occur if over all densities, kinetic fragility is represented by a single number.

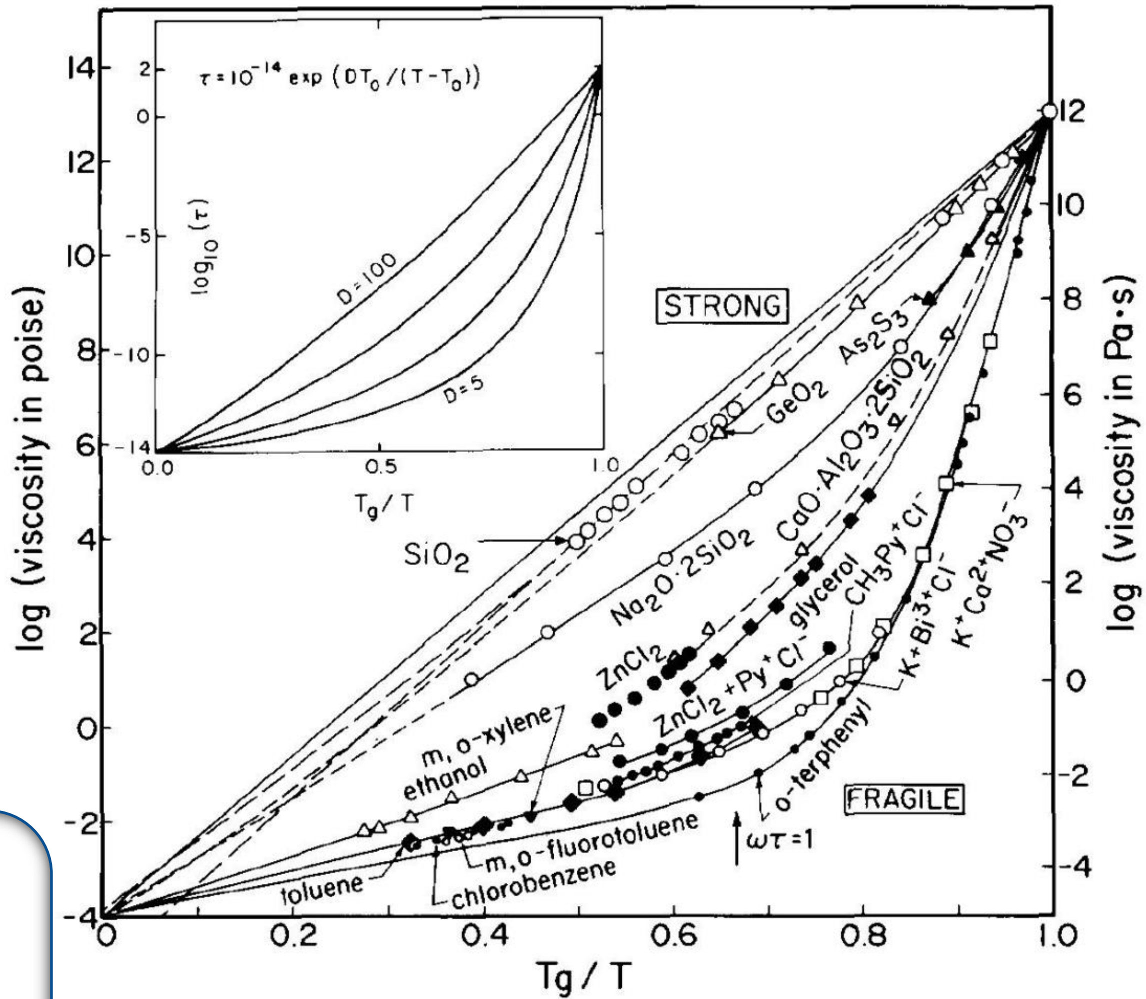
Kinetic fragility

- How rapidly timescales of structural relaxation increases as a liquid is supercooled

Global measure (using VFT)

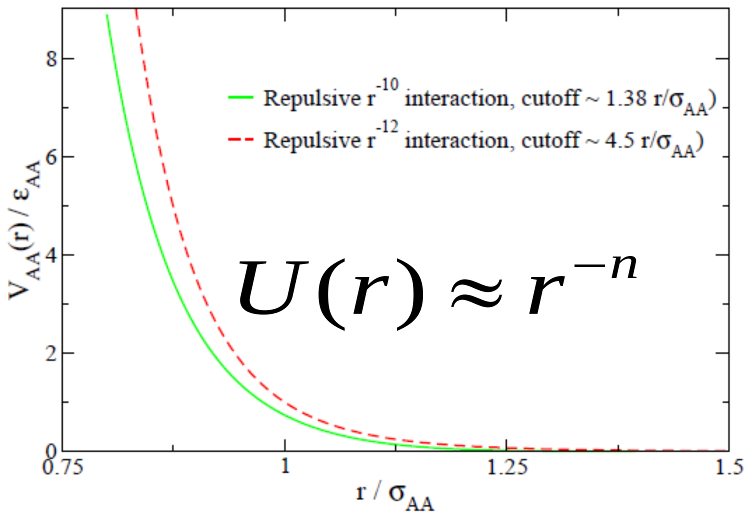
$$\tau = \tau_0 \exp\left[\frac{1}{K_{\mathrm{VFT}}(\frac{T}{T_{\mathrm{VFT}}} - 1)}\right]$$

$$(D_A)^{-1} = (D_A)_0^{-1} \exp\left[\frac{1}{K_{\mathrm{VFT}}(\frac{T}{T_{\mathrm{VFT}}} - 1)}\right]$$



C. A. Angell, J. Non-Cryst. Solids, 131-133, 13 (1991).

Density temperature (DT) scaling : inverse power law (IPL) liquids



1. Virial proportional to potential energy

$$U(r) \approx r^{-n}$$

$$\Rightarrow W = \frac{1}{d}\left(\sum_i \vec{r}_i \cdot \frac{\partial}{\partial \vec{r}_i}\right)U = \frac{n}{d}U$$

d = dimension of space

2. Density and temperature related in canonical probability

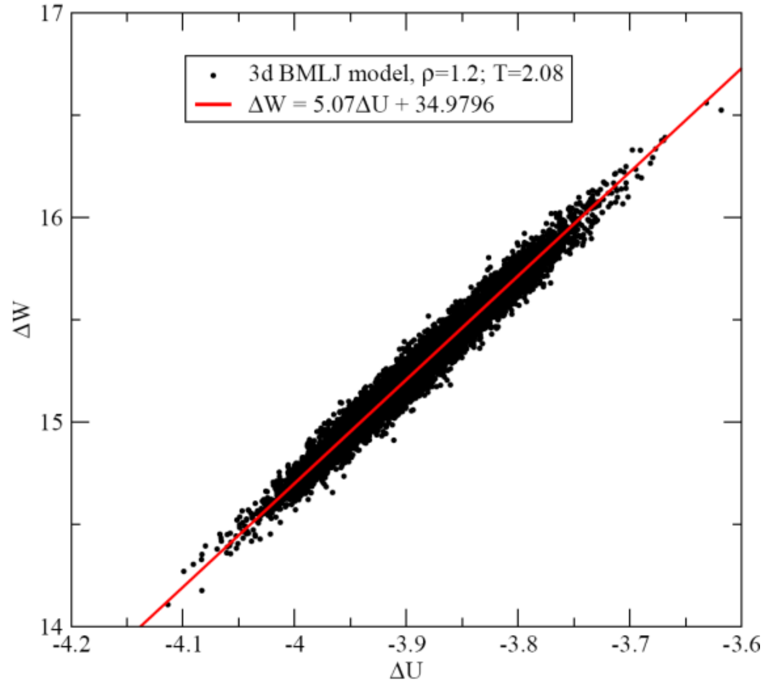
$$\beta U = f\left(\frac{\rho^{\frac{n}{d}}}{T}\right)$$

3. Dynamics function of combination of density and temperature

$$\tau(\rho,T) = \tau\left(\frac{\rho^{\frac{n}{d}}}{T}\right)$$

DT scaling : *non*-IPL liquids

Recent analyses found in certain **non – IPL** liquids (e.g. liquids dominated by Van der Waals interaction) :



1. Virial (W) and PE (U) are **strongly correlated**.

2. Canonical probability at two different state points (ρ_1, T_1) and (ρ_2, T_2) are proportional (**isomorphism**)

$$\exp\left(-\frac{U_1}{k_B T_1}\right) = C_{12}\exp\left(-\frac{U_2}{k_B T_2}\right)$$

3. Relaxation times at different densities (pressures) and temperatures collapse on a master curve i.e. **show density temperature scaling** with scaling exponent *predicted* from virial – energy correlation

$$\tau(\rho, T) = \tau\left(\frac{h(\rho)}{T}\right)$$

$$h(\rho) = \rho^{\gamma}$$

$$\gamma = \frac{\langle \Delta W \Delta U \rangle}{\langle (\Delta U)^2 \rangle}$$

Simulation details

- NVT MD simulation of Kob – Andersen binary mixture* ($A_{80}B_{20}$)
- System size N = 1000,

  Time step dt = 0.001 – 0.005

- 3 – 5 independent runs of length at least 100 α relaxation times for each state point

Density	Temperature range	Onset Temperature
1.10	0.28 - 2.0	
1.15	0.34 – 2.0	
1.20	0.435 – 2.0	
1.25	0.52 – 2.0	
1.35	0.77 – 2.0	

*W. Kob and H. C. Andersen, Phys. Rev. E, 51, 4626 (1995).

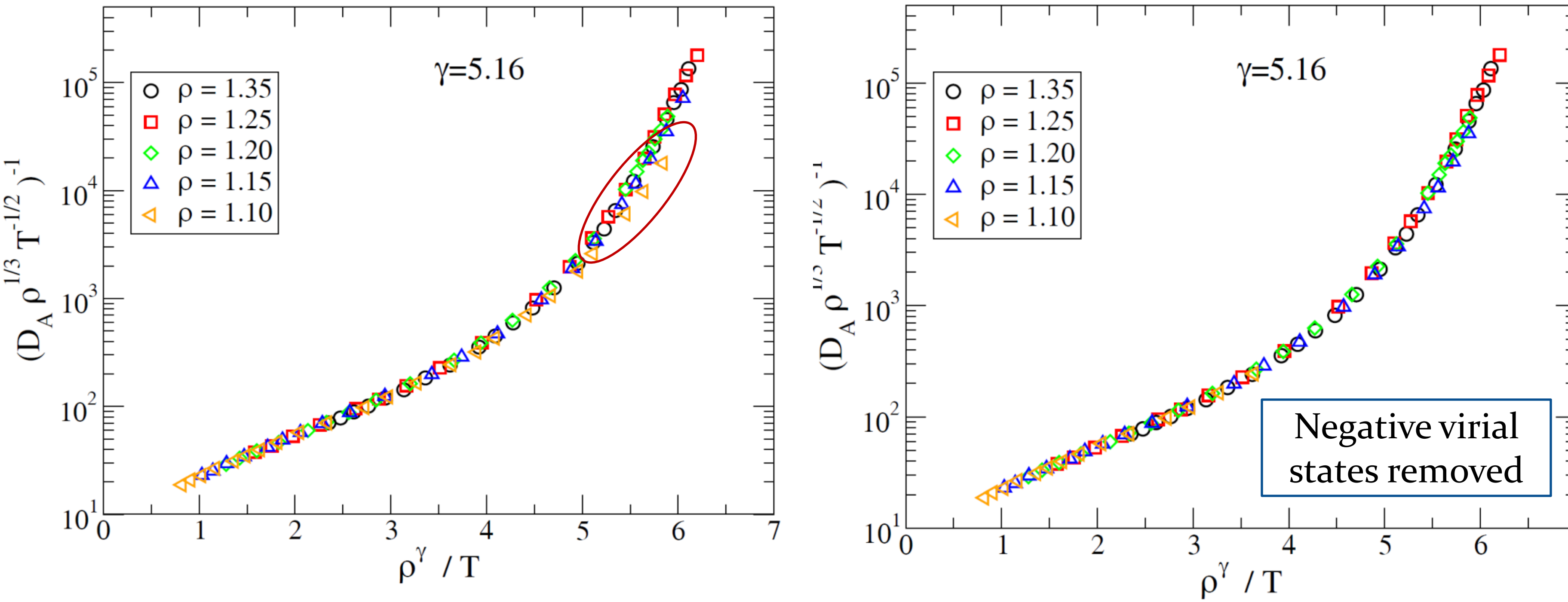
What quantities to analyze ?

✓Diffusivity of bigger (A) particles from mean squared displacements

✓α relaxation time from overlap functions

✓ Configurational entropy from difference of total and basin (vibrational) entropy

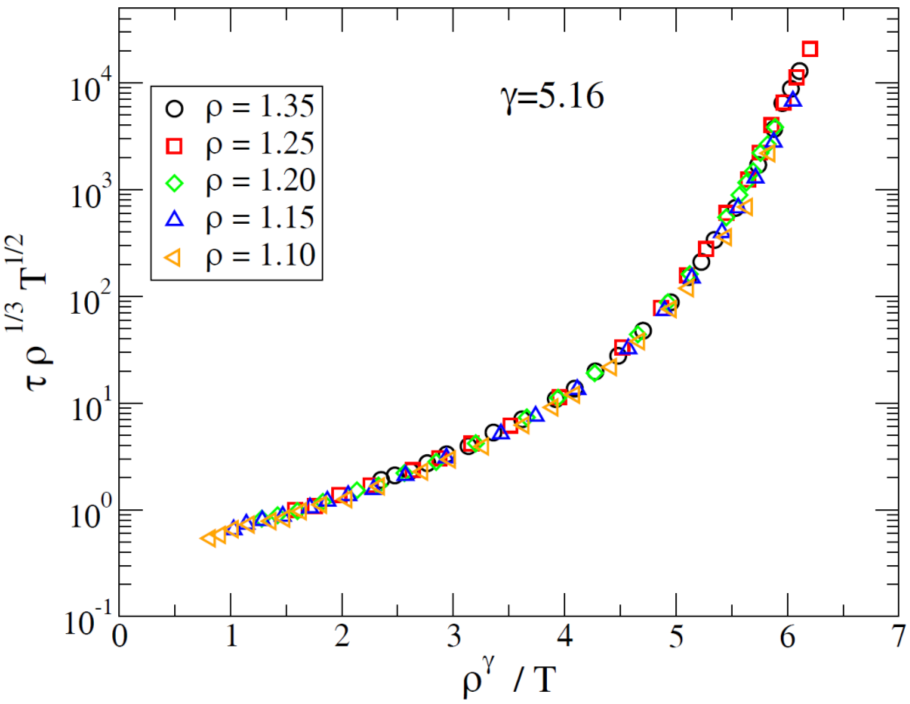
Result 1 : DT scaling of timescale - diffusivity

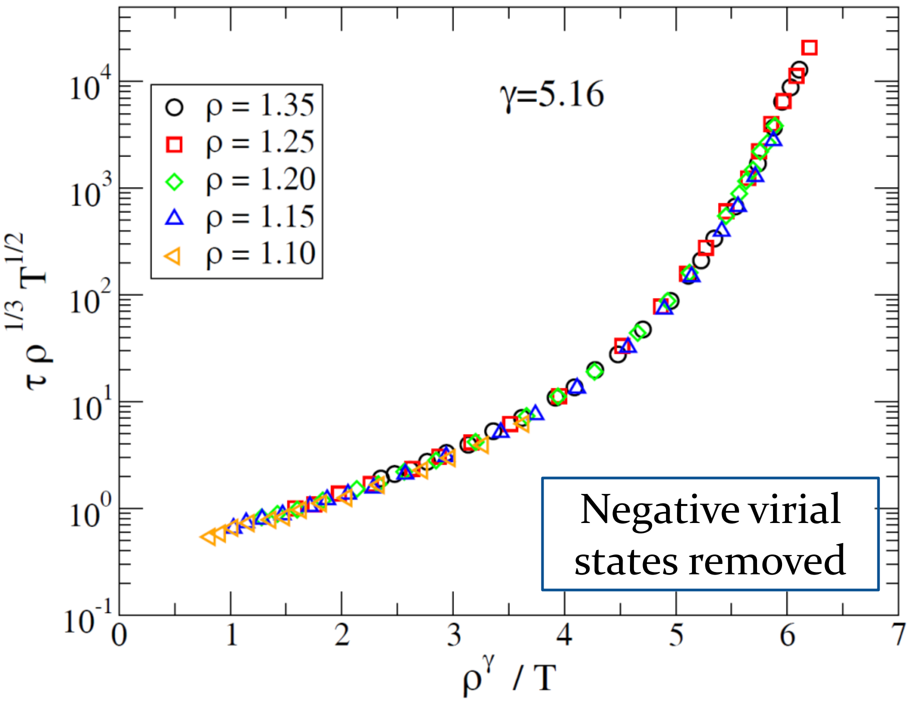


- Diffusivity show impressive DT scaling. Data collapse improves if negative virial states are removed.
- Remark 1: Need to compare with the DT scaling of thermodynamic quantity.
- Remark 2: Scaling exponent is *predicted** from strong correlation between virial and potential energy.

*U.R. Pedersen, T.B. Schroder and J.C. Dyre, Phys. Rev. Lett., 105, 157801 (2010).

Result 1 : DT scaling - α relaxation time

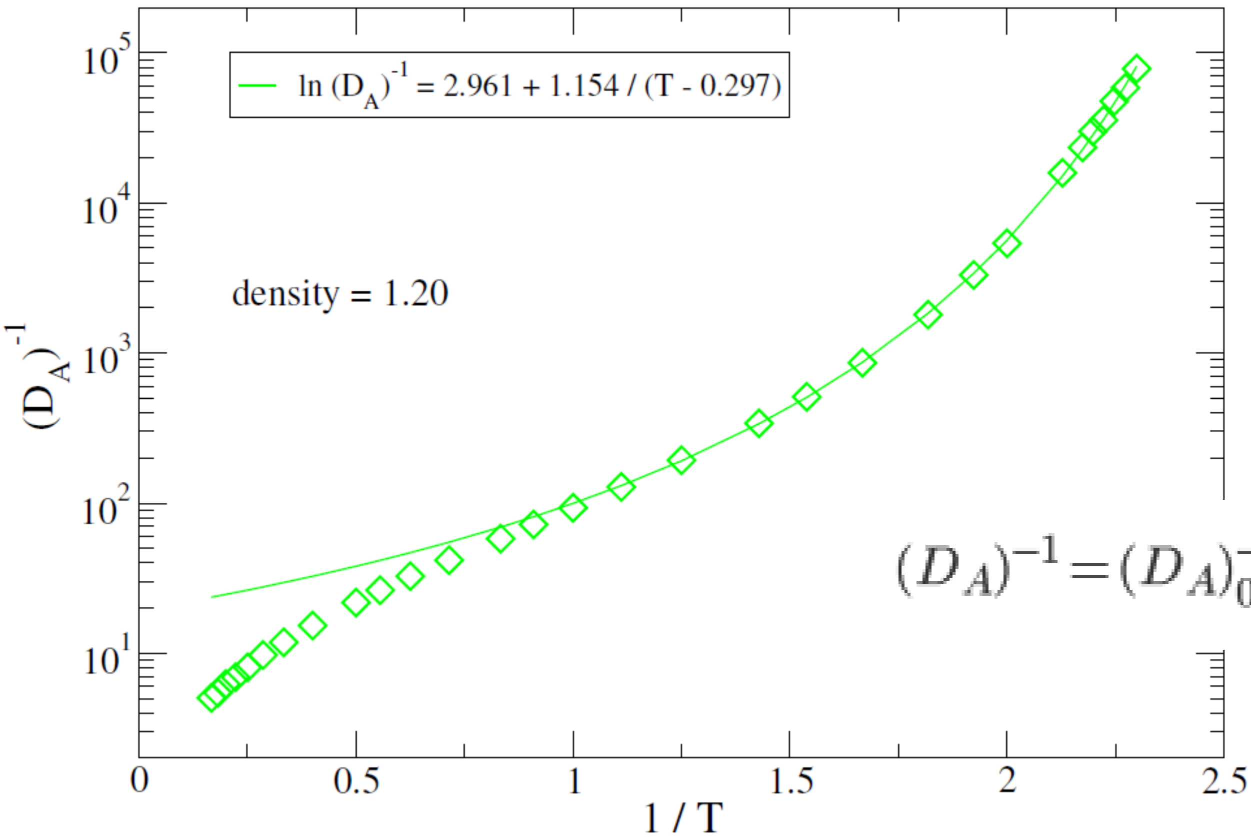




- Structural relaxation time also show impressive DT scaling.

Is kinetic fragility independent of density ?

- The very good data collapse suggests that kinetic fragility is independent of density. We test this hypotheses carefully.

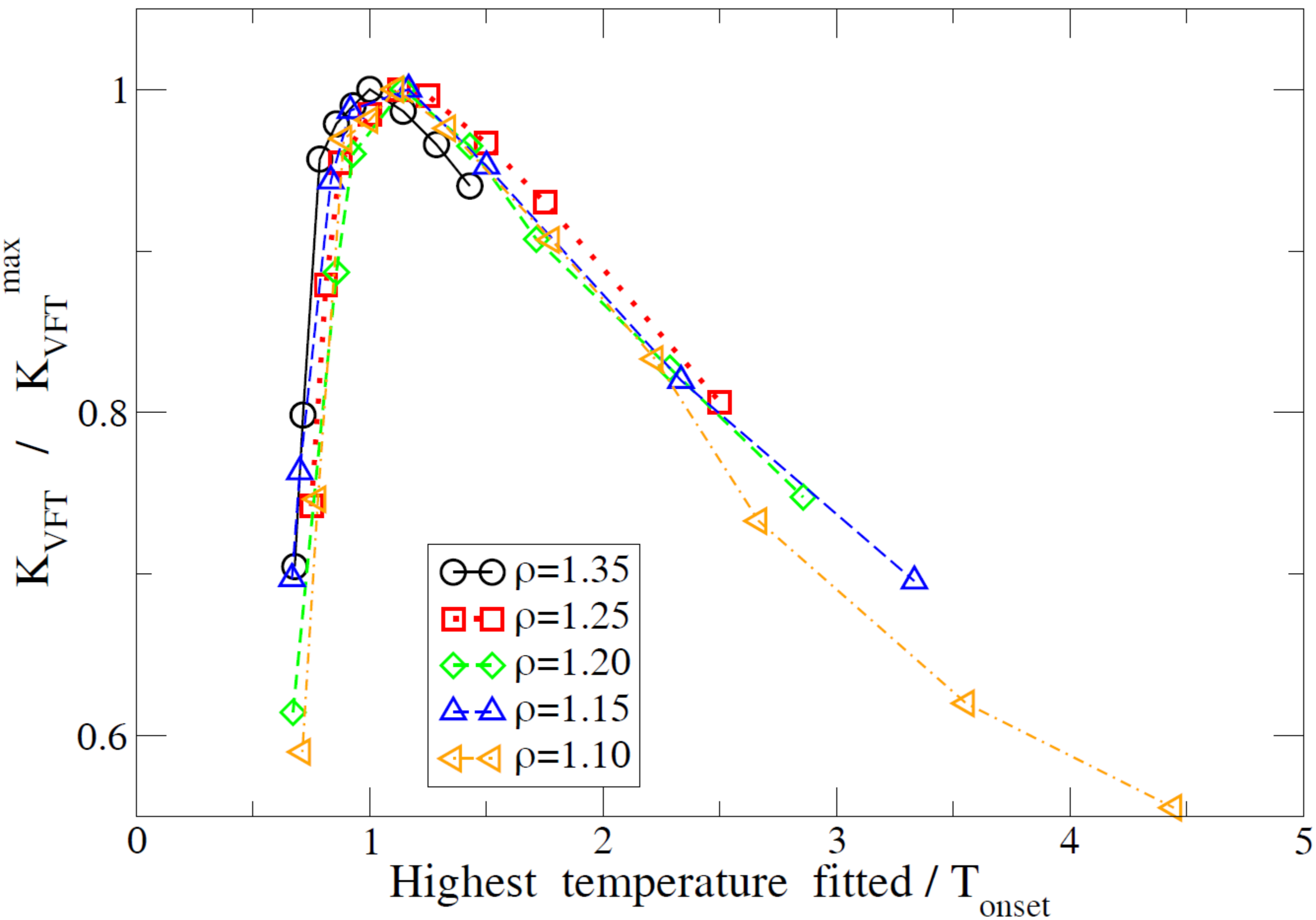


- Compute kinetic fragility at different densities from **direct VFT fit**

$$(D_A)^{-1} = (D_A)_0^{-1} \exp\left[\frac{1}{K_{\mathrm{VFT}}\left(\frac{T}{T_{\mathrm{VFT}}} - 1\right)}\right]$$

VFT fit looks good but…

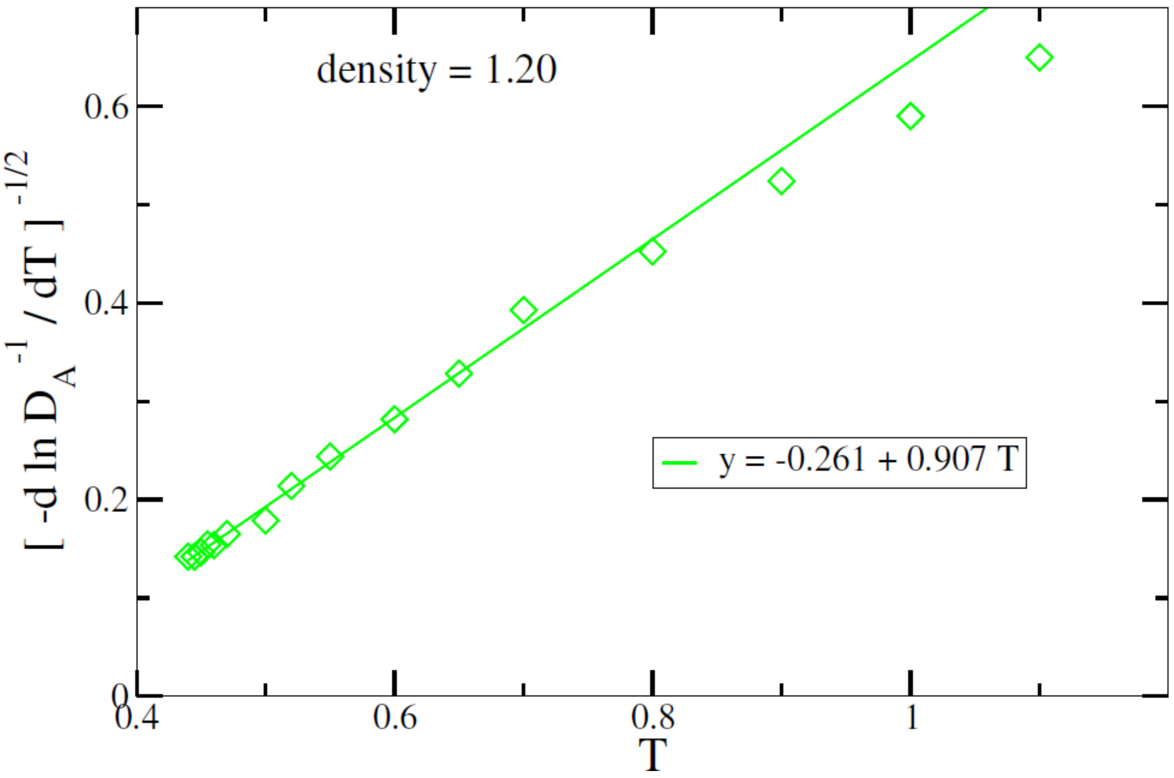
- Estimate of kinetic fragility *depends on the range of temperature fitted*
- We choose to fit upto the onset temperature



Stickel analysis of diffusivity data

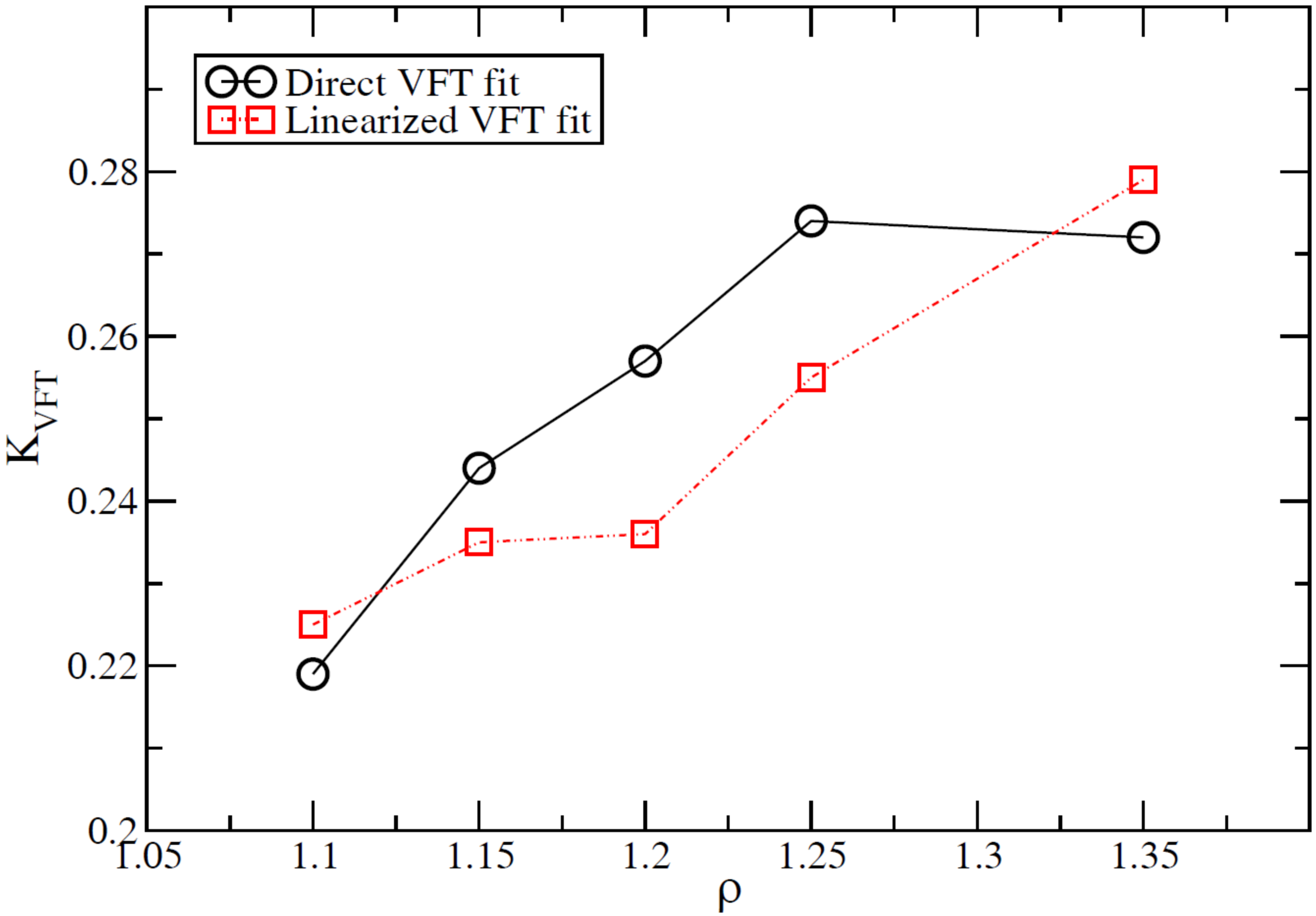
Linearized VFT fit

$$\left[-\frac{d\ln D_A^{-1}}{dT}\right]^{-1/2} = \sqrt{\frac{K_{VFT}}{T_{VFT}}}\,T - \sqrt{K_{VFT}T_{VFT}}$$



- Low T data is indeed linear and hence reliable.

Result 2 : Density dep. of kinetic fragility is weak … but non zero

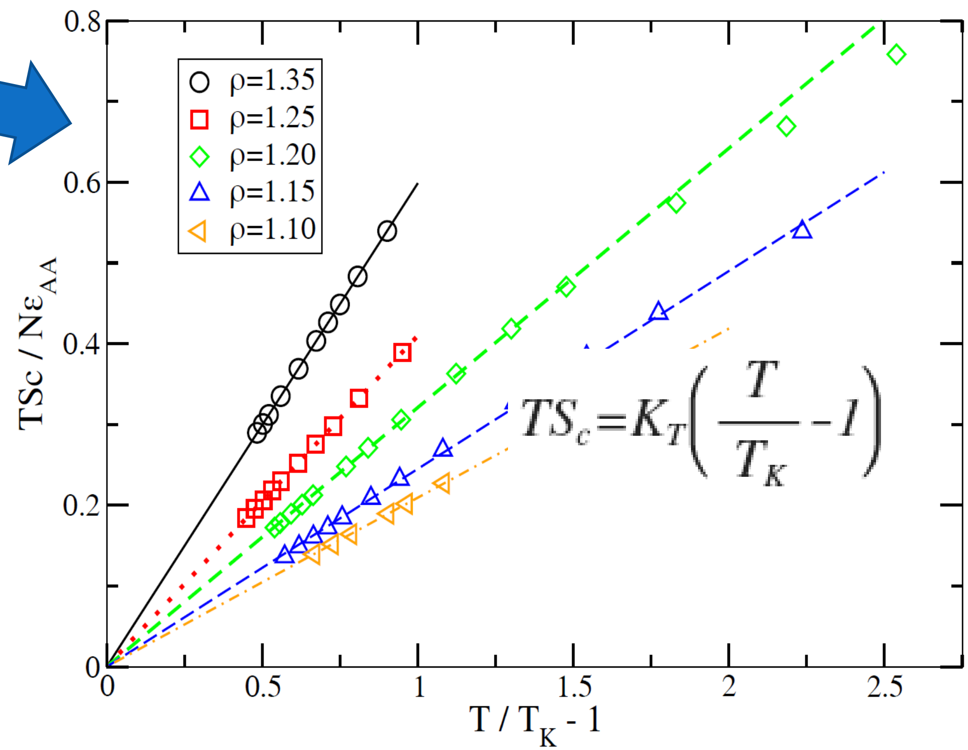


Rationalizing density dep. of kinetic fragility: connect to thermodynamics

- **Adam Gibbs relation**

$$D_A^{-1} = (D_A)_0^{-1} \exp\left[\frac{A}{TS_c}\right]$$

- **Thermodynamic fragility (K_T):** for a potential energy landscape with Gaussian distribution of energy minima and harmonic basins, TS_c is linear in temperature*



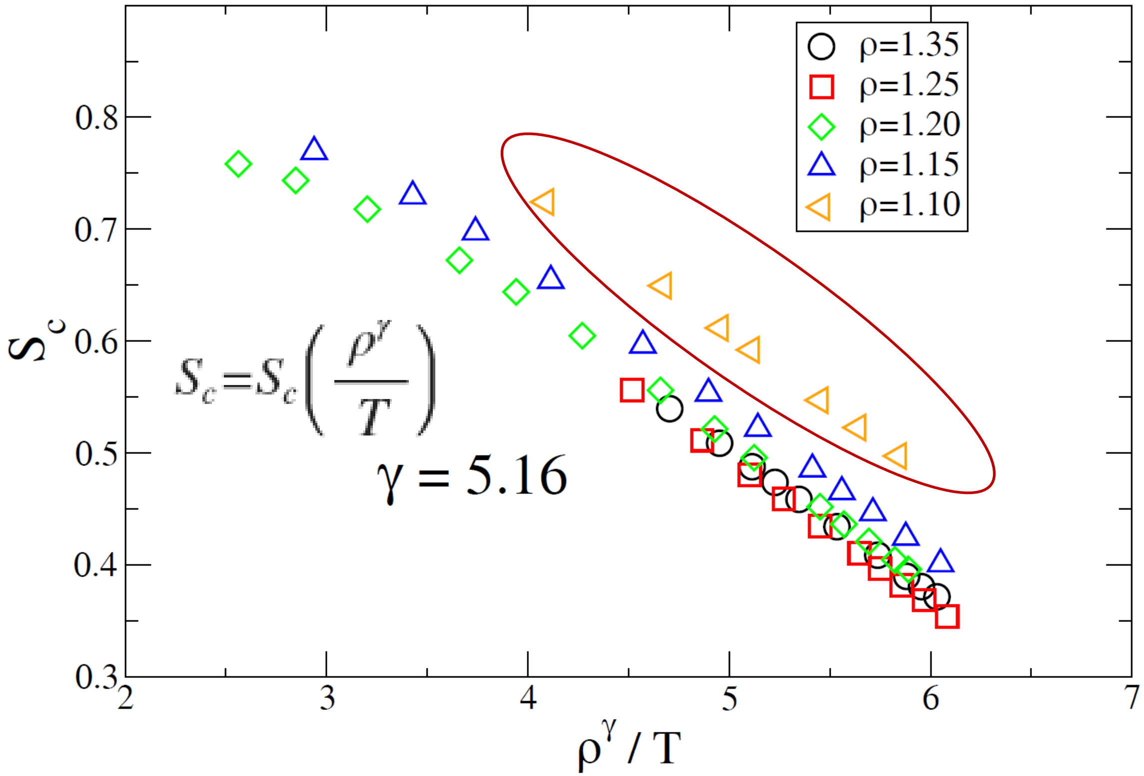
- Combining VFT and AG and assuming $T_{VFT} \sim T_K$, resolve kinetic fragility into two parts

$$K_{AG} = \frac{K_{VFT}}{A}$$

*S. Sastry, Nature, 409, 164, (2001).

Result 3 : DT scaling of configuration entropy

- For non-IPL liquids showing strong virial-energy correlation, configuration entropy predicted* to show DT scaling.



- S_c shows reasonably good data collapse. Data collapse improves if negative virial states are removed.

* N. Gnan *et al.*, J. Chem. Phys. 131, 234504 (2009).

Consequences of DT scaling of entropy

✓ From DT scaling of diffusivity and VFT law, **thermodynamic fragility K_T has power law density dependence**

$$D_A^{-1} = (D_A)_0^{-1} \exp\left[\frac{A}{TS_c}\right]$$

$$S_c = S_c\left(\frac{\rho^\gamma}{T}\right)$$

$$TS_c = K_T\left(\frac{T}{T_K} - 1\right)$$

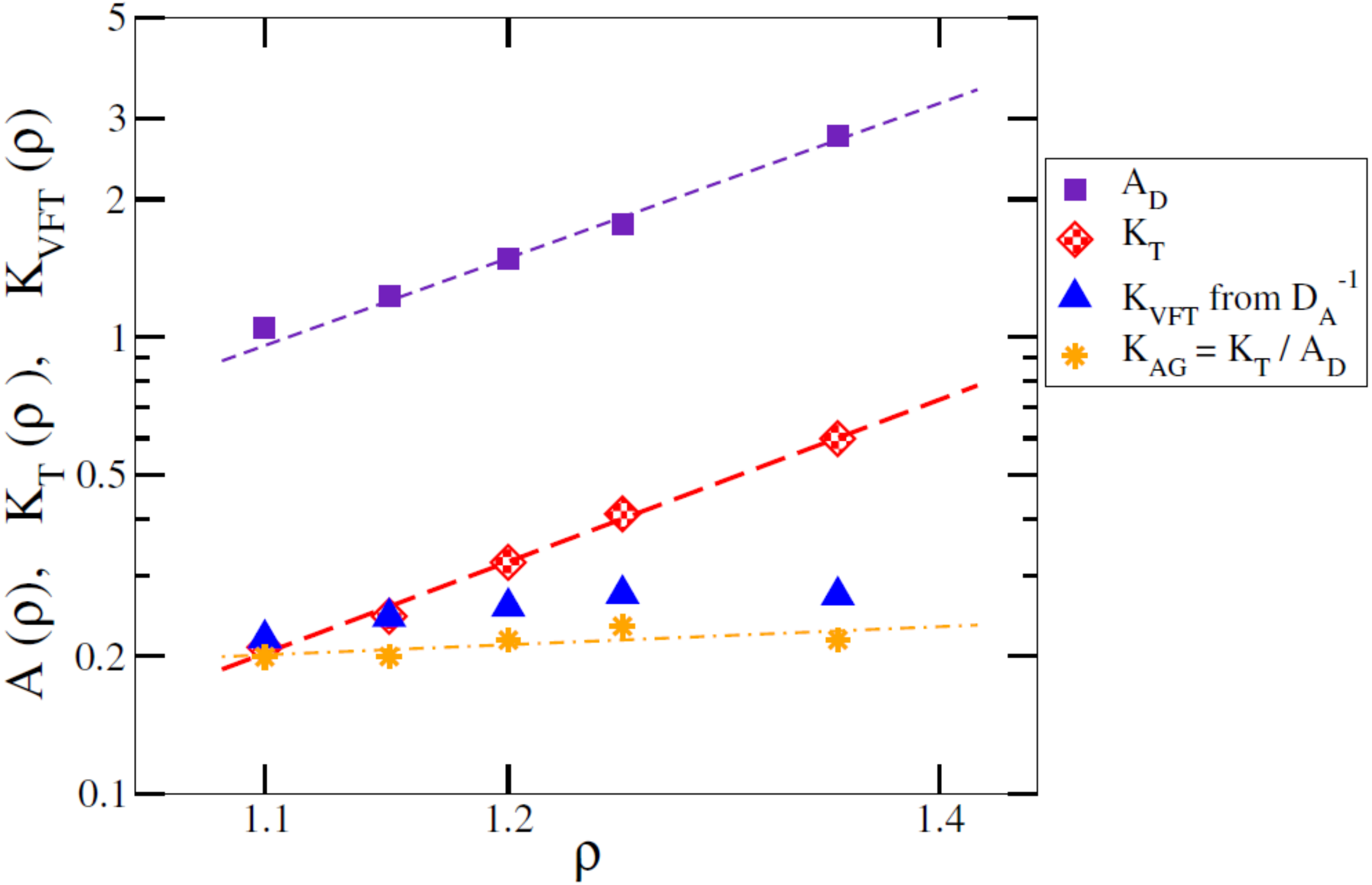
✓ From AG relation and DT scaling of diffusivity, **AG coefficient A has power law density dependence**

✓ If the exponents γ_1 and γ_2 are approximately same, then $K_{AG} = K_T / A$ can have weak but non zero density dependence

$$K_T \sim \rho^{\gamma_1}$$

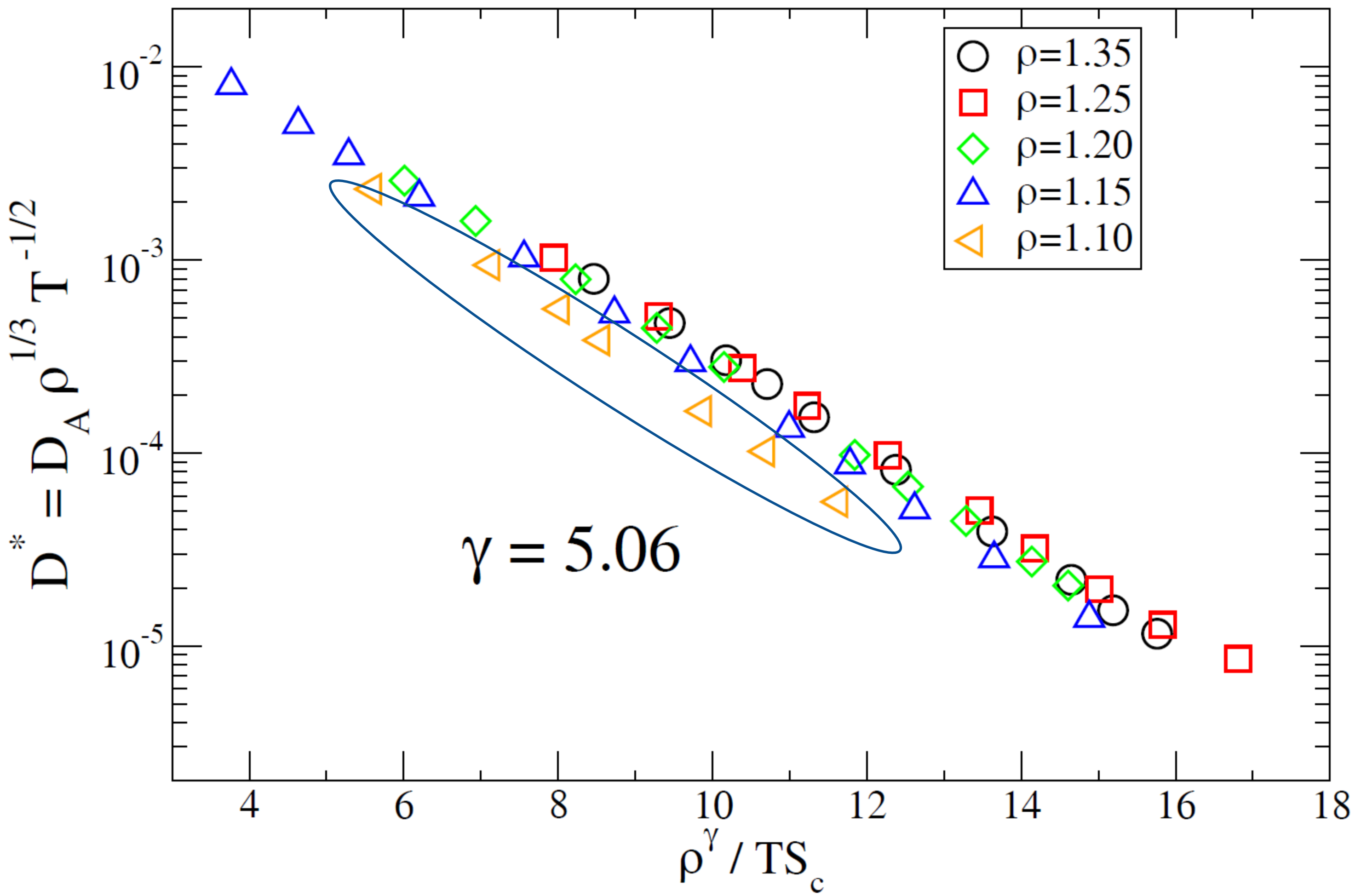
$$A \sim \rho^{\gamma_2}$$

Result 4 : Rationalizing the density dep. of kinetic fragility



- Power law density dependence for A, K_T (except at lowest density) .
- Exponents for A, K_T are similar. Hence the density dependences cancel each other . Hence the density dep. of kinetic fragility is weak.

Result 5 : DT scaling of AG relation



❖ Scaling exponent 5.06 from density dependence of AG coefficient A

Data collapse improves if negative virial states are removed.

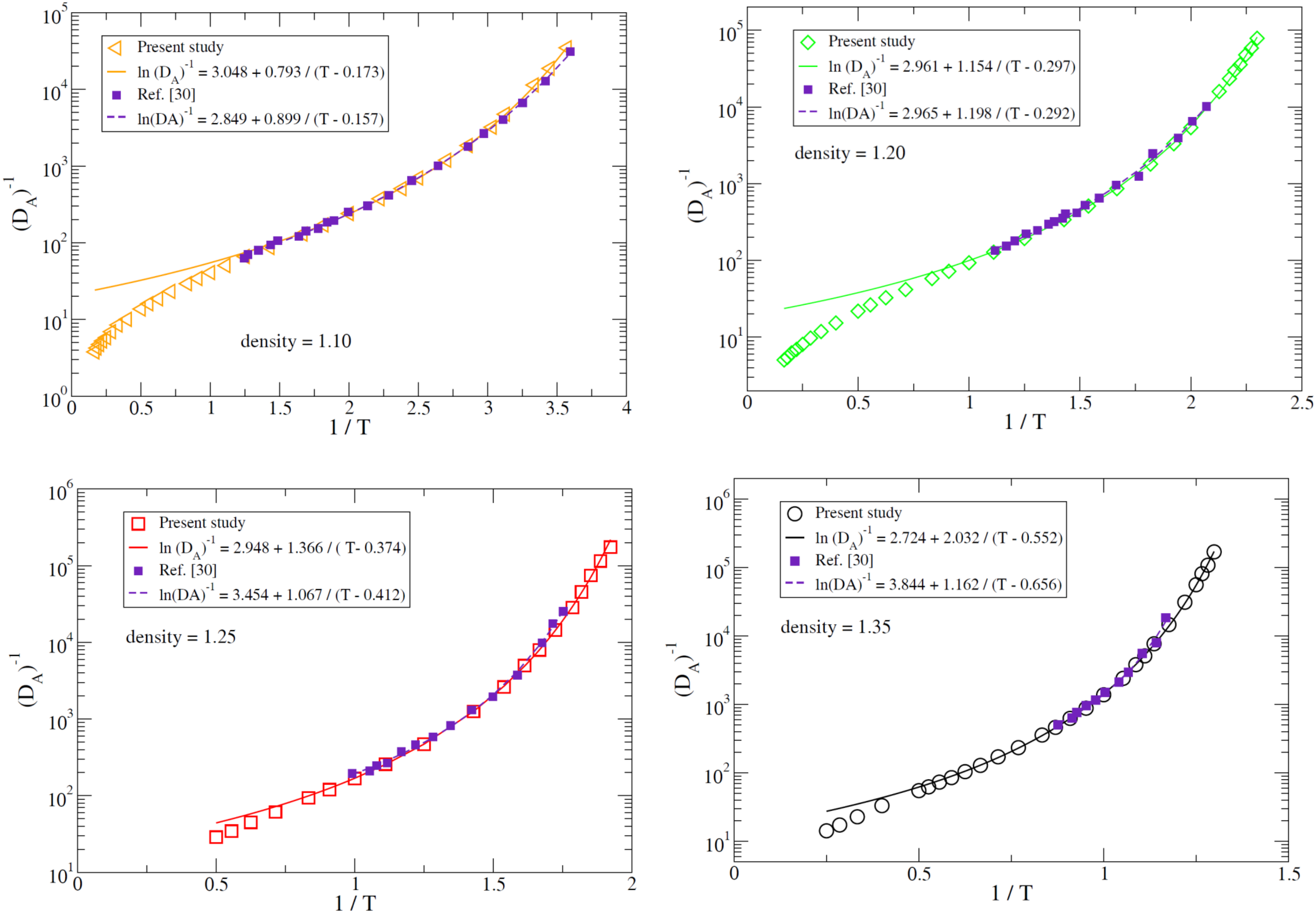
Conclusions

- Diffusivity and relaxation time for KA model show DT scaling and the quality of data collapse improves if the negative virial states are excluded.
- Kinetic fragility is not independent of density, but the density dependence is weak.
- This weak density dependence can be understood in terms of DT scaling and deviations from DT scaling at low densities.
- The Adam-Gibbs (AG) relation exhibits DT scaling at high densities.

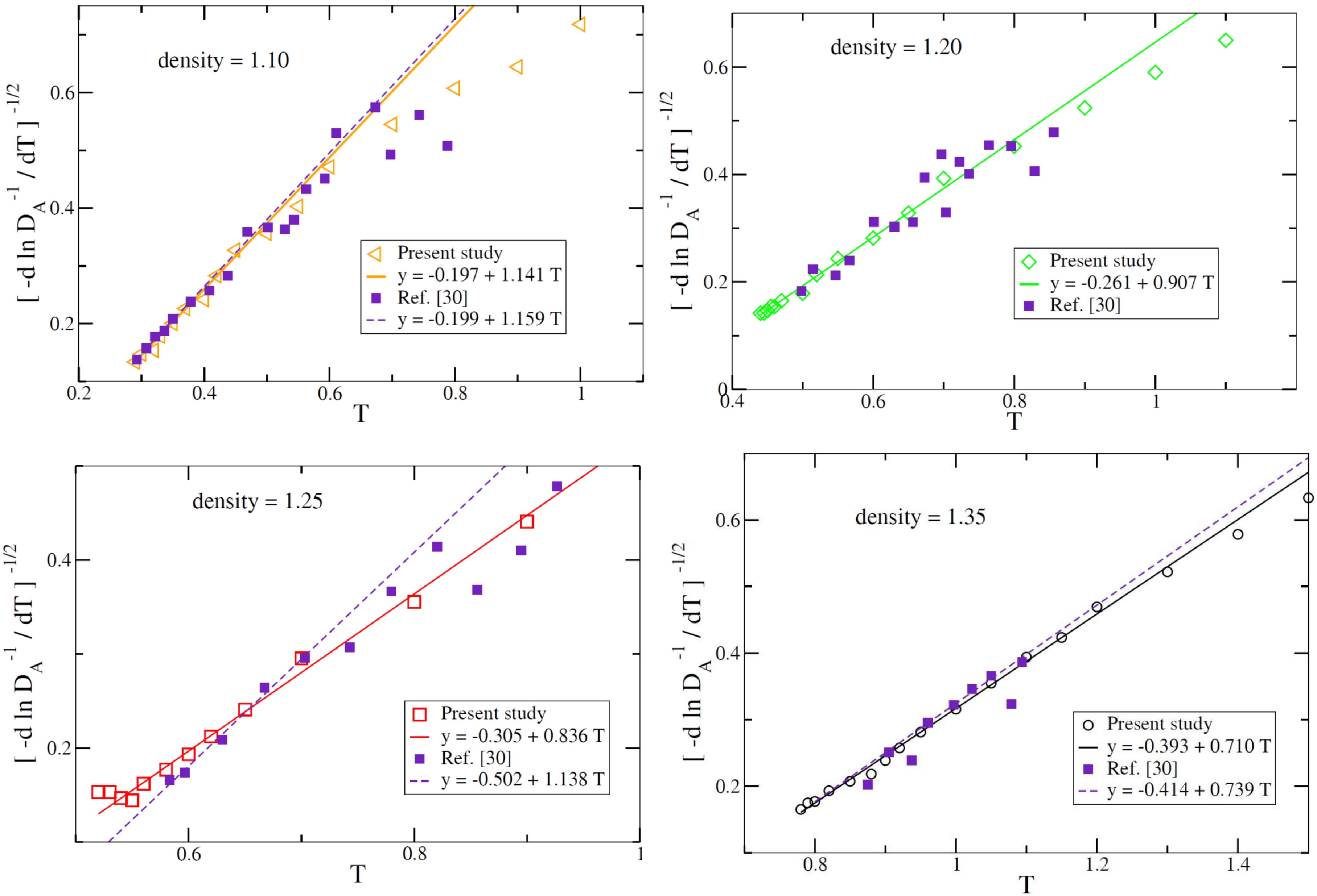
Thanks for the attention !!

Comparison with previous work

Comparison of raw data and direct VFT fit



Comparison of Stickel fit



Comparison of fragility values