The role of attractive interaction on the thermodynamic fragility

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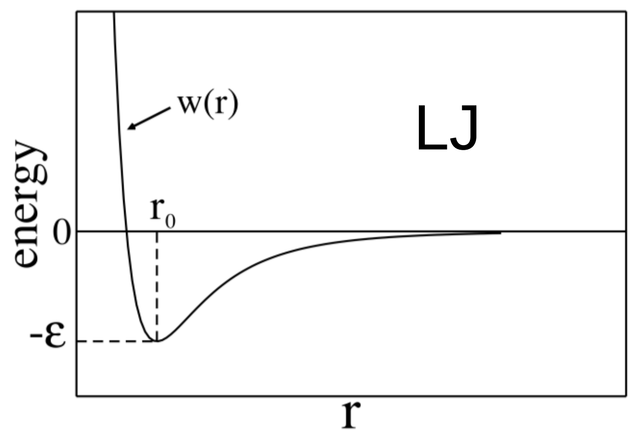
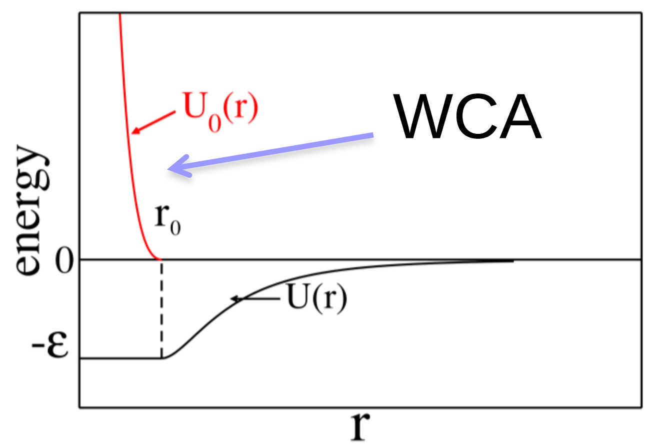
Historically → Role of attractive forces

van der Waals picture → Dominant role of short ranged harshly repulsive intermolecular forces → hard sphere
→ Attractive forces provide a homogeneous background

van der Waals equation of state 1873

Weeks – Chandler – Anderson → Perturbative treatment of the attractive part

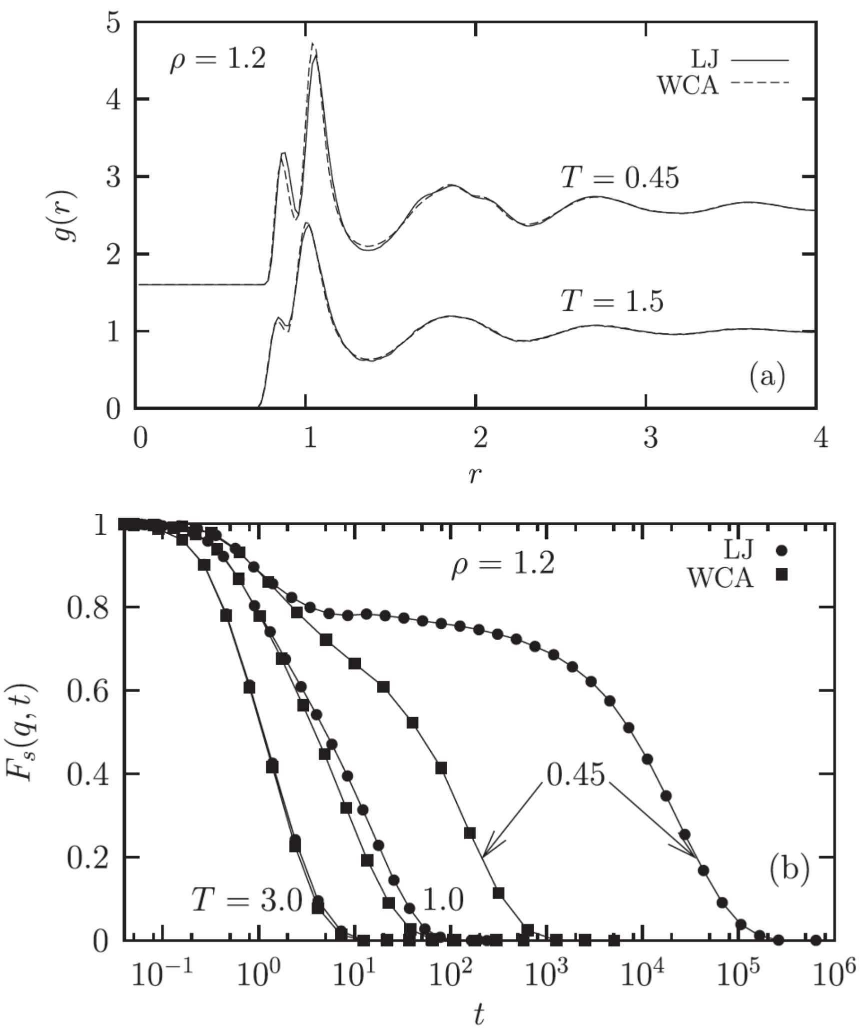




Birth of WCA potential

Weeks, Chandler , Anderson, J. Chem. Phys. 54 5237 (1971)

Perturbative or Nonperturbative ??



System- K-A model

80:20 binary mixture

σ_A=1.0 σ_B=0.88 σ_{AB}=0.8

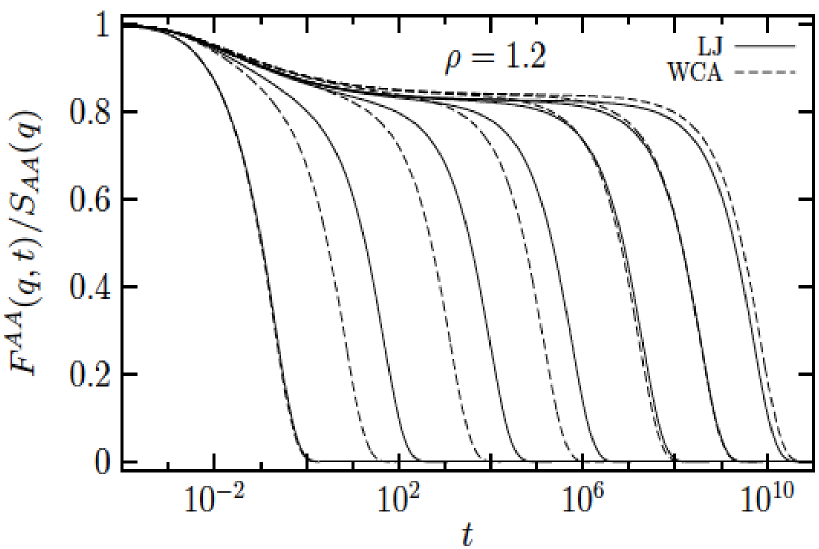
ε_{AA}=1.0 ε_{BB}=0.5 ε_{AB}=1.5

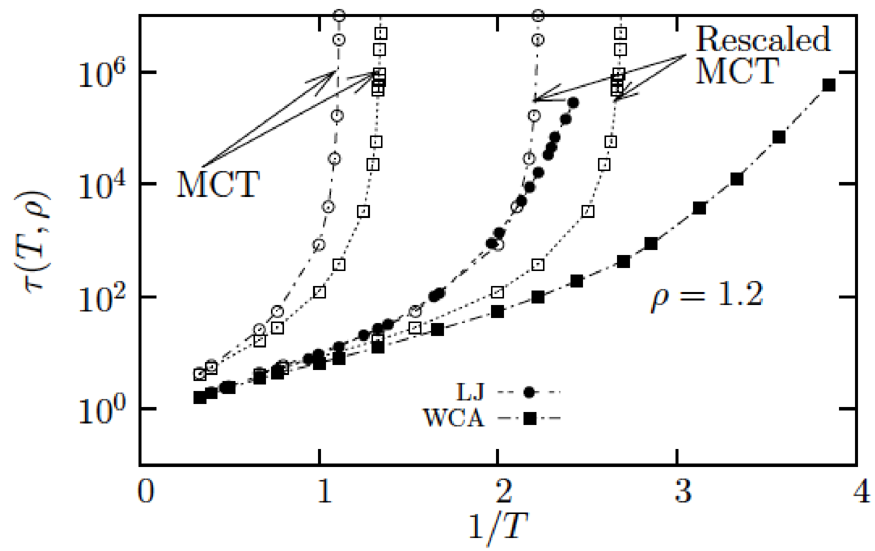
Small difference in g(r) at high and low T → supports perturbative argument

Large difference in dynamics at low T → supports nonperturbative argument

Berthier & Tarjus, PRL **103**, 170601 (2009); PRE **82**, 031502 (2010); EPJE 34, 96 (2011) ; JCP 134, 214503 (2011)

Mode coupling theory (MCT) prediction





MCT fails to predict simulated results

•Over estimated the temperature regime for slow dynamics

•Failed to predict the difference between the LJ and WCA system

Berthier & Tarjus, PRE **82**, 031502 (2010)

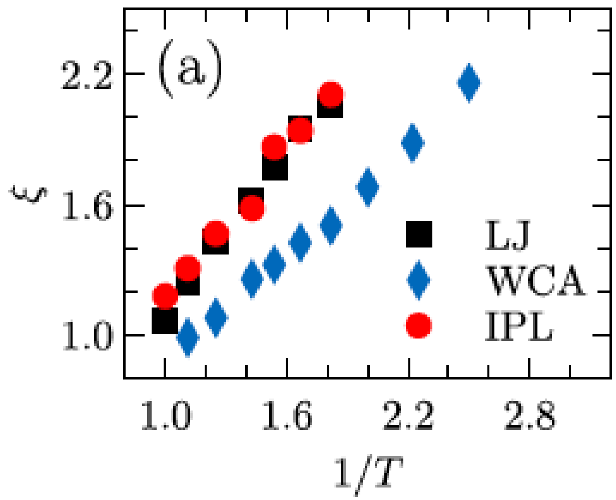
How a small difference in structure can account for a large difference in dynamics??

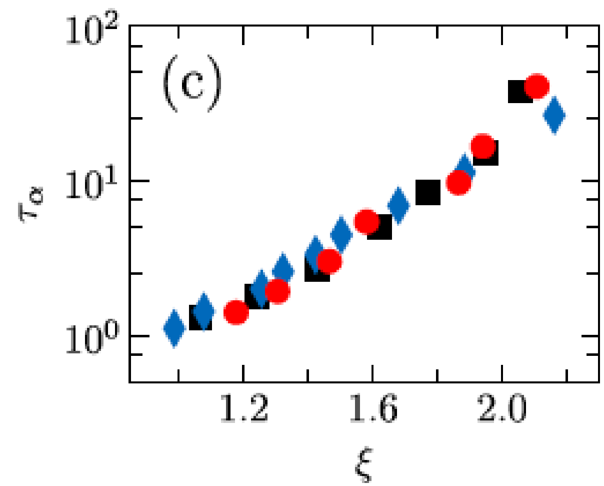
- Is the slow down of relaxation time purely kinetic in nature ?? → supports kinetically constraint model (Chandler and Garrahan , PNAS **100** , 9710 (2003))
- Difference in static pair correlation is small but can many body (higher order) static correlations explain the difference in dynamics ?? Coslovich PRE **83**, 051505 (2011)

Origin of slow dynamics → Kinetic or Thermodynamic ?

Growing thermodynamic point–to-set (PTS) length scale correlates with growing relaxation time

Hocky, Markland and Reichman PRL,**108**, 225506 (2012)





“The mere existence of a growing **PTS is not in contradiction** with a picture based on kinetically constrained models”

Configurational entropy as the thermodynamic marker

Thermodynamic & Kinetic fragility

Ito, Moynihan & Angell **398,** 492 (1999) : Angell , Nature **410**, 663 (2001): Sastry , Nature 409 , **164** (2001)

Kinetic fragility from dynamics

Vogel –Fulcher- Tammann (VFT) equation

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

Kinetic index of fragility

Thermodynamic fragility from configurational entropy

$$S_c = \int_{T_K}^{T} \Delta C_P / T \, dT \qquad \Delta C_P = K_T / T$$

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

Thermodynamic index of fragility

What is the relation between kinetic & thermodynamic fragility ?

Adam –Gibbs expression relates the dynamics to the configurational entropy → to the energy landscape

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

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

Temperature independent S_c

↓

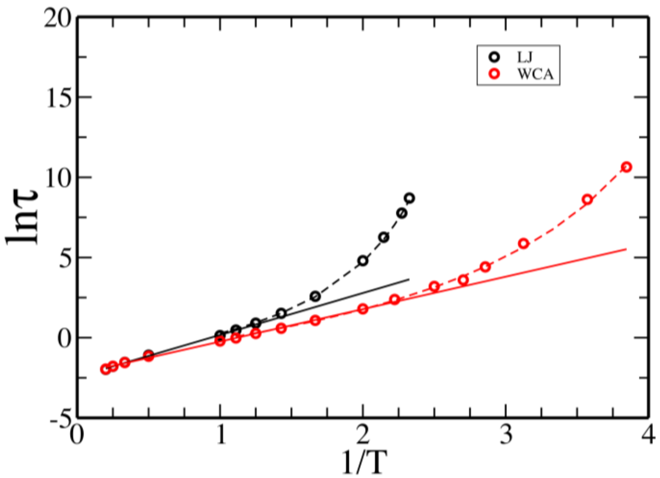
AG expression → Arrhenius equation

AG parameter "A" related to high T activation energy E_o

Compare with VFT

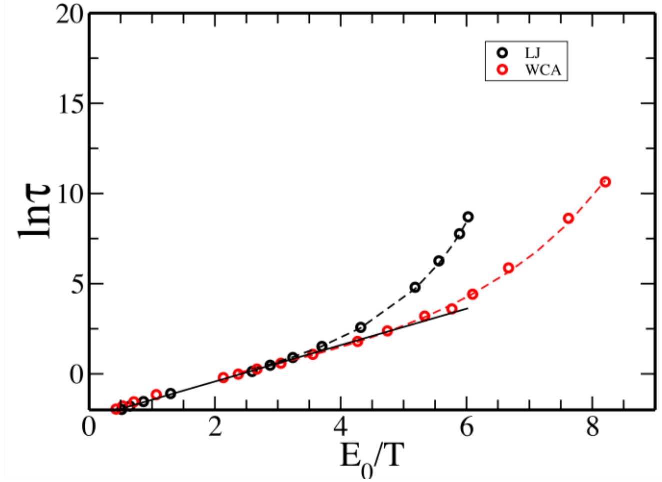
$$T_{VFT} = T_K \qquad K_{VFT} = K_T / A$$

Kinetic Fragility



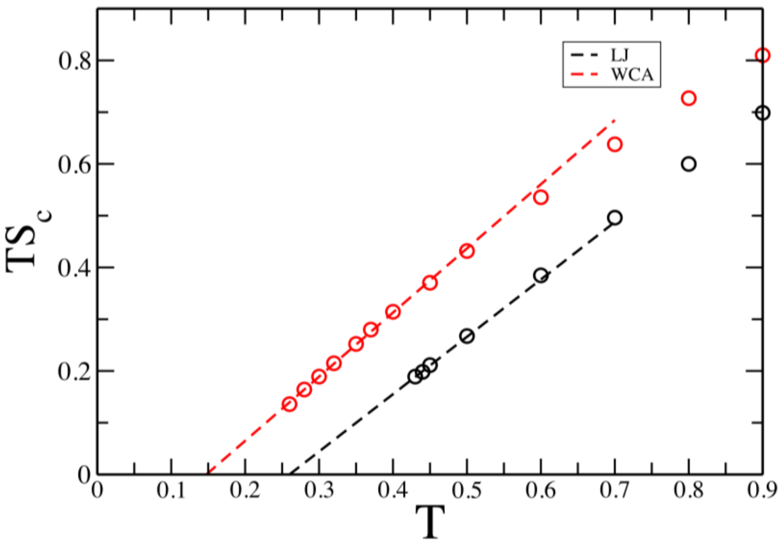
High T → LJ higher activation energy

LJ → more fragile liquid

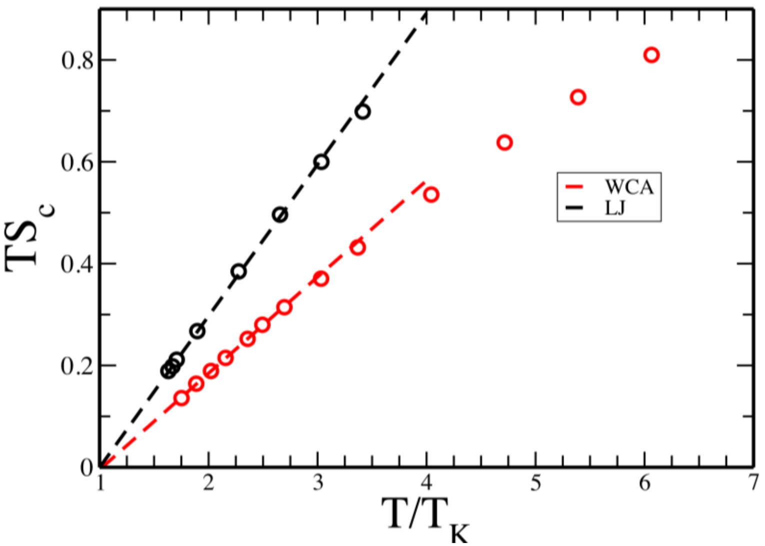


System	E_0	K_{VFT}	T_{VFT}
LJ	2.59	0.202615	0.291726
WCA	2.13	0.16478	0.173452

Thermodynamic Fragility

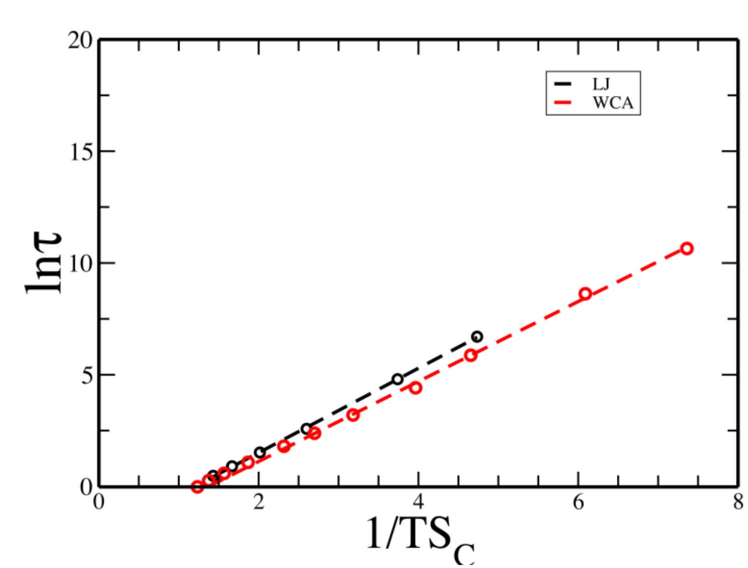


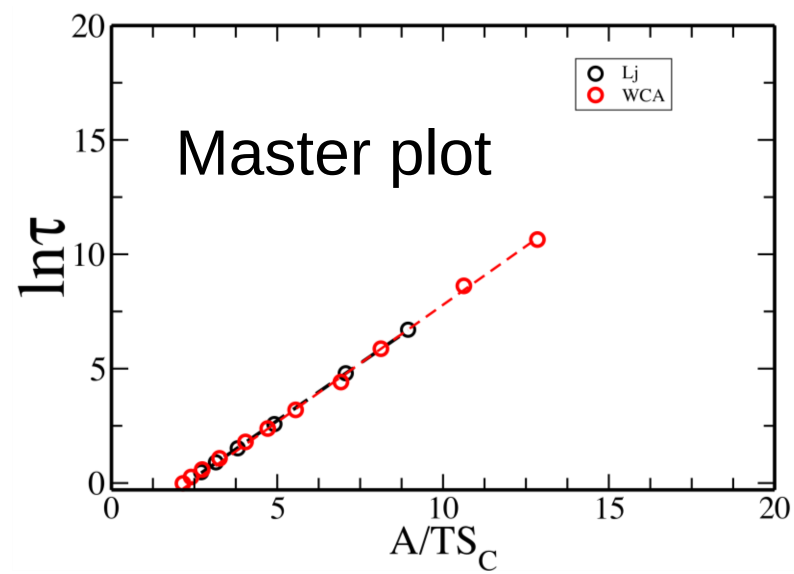
$$S_C = S_{ideal} + S_{ex} - S_{vib}$$



System	K_T	T_K
LJ	0.297947	0.2636
WCA	0.1892	0.1484

Adam–Gibbs relation
Thermodynamic vs. Kinetic fragility





system	K_{VFT}	A	K_T	$K_{AG}=K_T/A$
LJ	0.20262	1.8899	0.2980	0.1585
WCA	0.16478	1.7455	0.1892	0.1084

Thermodynamic fragility leads to kinetic fragility

Origin of difference in dynamics between LJ and WCA system

Facts :

- The pair structures are similar

- Significant difference in three-body correlation

- LJ mixture has more pronounced local ordering

Coslovich PRE **83**, 051505 (2011)

- Point-to-set correlation length → static length scale larger for LJ

Hocky, Markland and Reichman PRL,**108**, 225506 (2012)

- LJ system has larger thermodynamic fragility

Higher order many particle correlation → thermodynamic fragility → kinetic fragility

Pair correlation is **not** blind to changes happening in the system

Configurational entropy per particle

$$S_C = S_{total} - S_{vib} = S_{ideal} + S_{ex} - S_{vib}$$

Excess entropy per particle

$$S_{ex} = S_{total} - S_{id} = S_2 + S_3 + ... = S_2 + \Delta S$$

ΔS → residual multi particle entropy (RMPE)

Two body excess entropy per particle

$$S_2 / k_B = -\frac{\rho}{2}\sum_{\alpha\beta} x_\alpha x_\beta \int d^3r \left[g_{\alpha\beta}(r) \ln\left[g_{\alpha\beta}(r) \right] - g_{\alpha\beta}(r) + 1 \right]$$

Two body contribution to the configurational entropy per particle

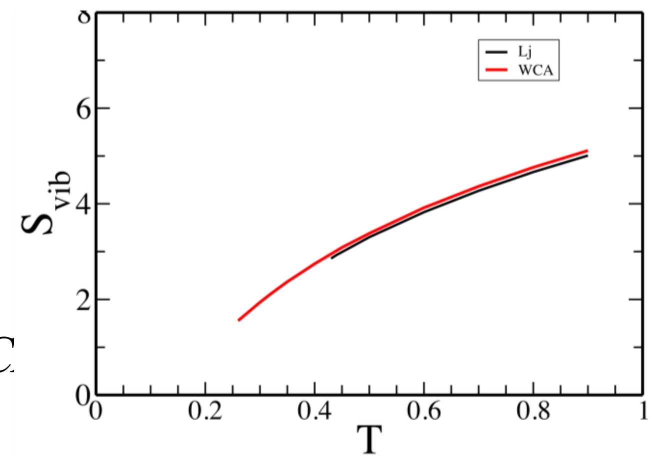
$$S_{C2} = S_{ideal} + S_2 - S_{vib}$$

What can we expect about S_{C2} ?

$$g(r)^{LJ} \approx g(r)^{WCA}$$

$$S_2^{LJ} \approx S_2^{WCA}$$

$$S_{vib}^{LJ} \approx S_{vib}^{WC}$$

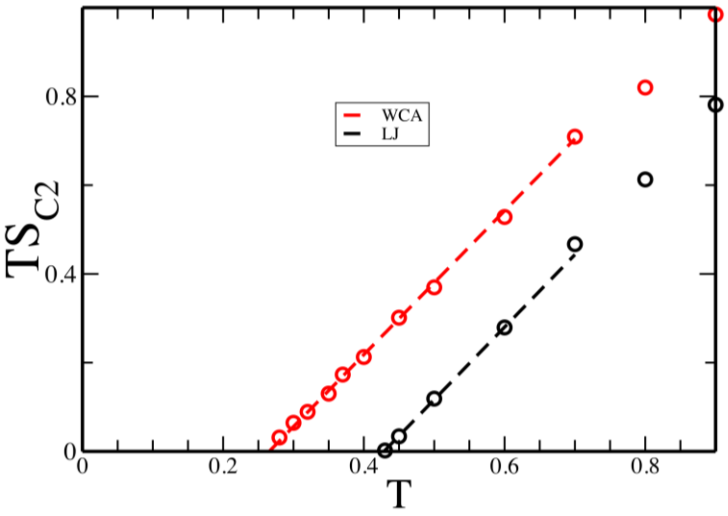


$$S_{C2}^{LJ} \approx S_{C2}^{WCA}$$

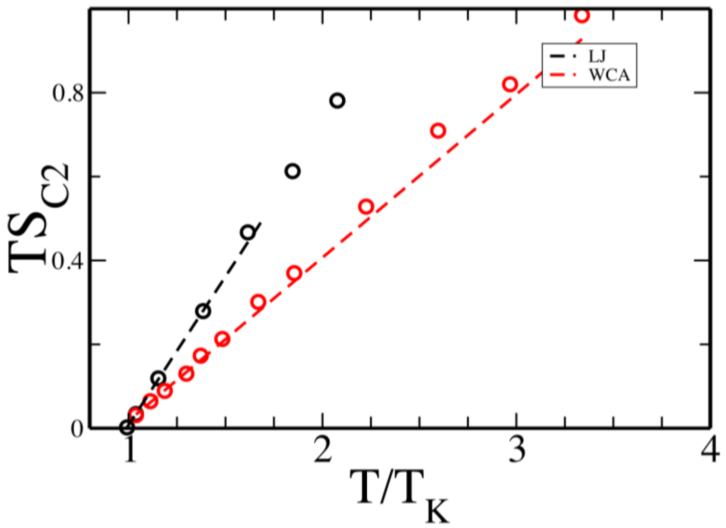
$$TS_{C2}^{LJ} \approx TS_{C2}^{WCA}$$

The two body contribution to the configurational entropy similar for LJ and WCA system

The reality about S_{C2}



Two body contribution to the configurational entropy different for LJ and WCA system



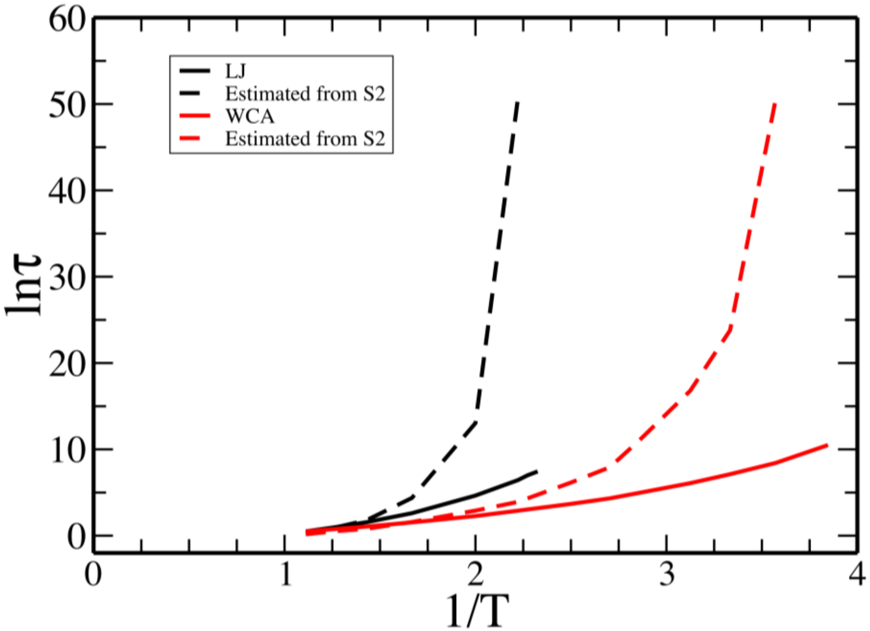
System	K_{T2}	T_{K2}
LJ	0.7078	0.433
WCA	0.3891	0.269

Even S_{C2} predicts higher thermodynamic fragility for LJ system

The effect on kinetic fragility

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

$$\tau_{est}(T) = \tau_0(T)\exp\left(\frac{A}{TS_{C2}}\right)$$



Estimated relaxation time

•Diverges faster → reflects MCT result

•Larger differences in Kinetic fragility between LJ and WCA system → different from MCT result

Pair correlation and Fragility

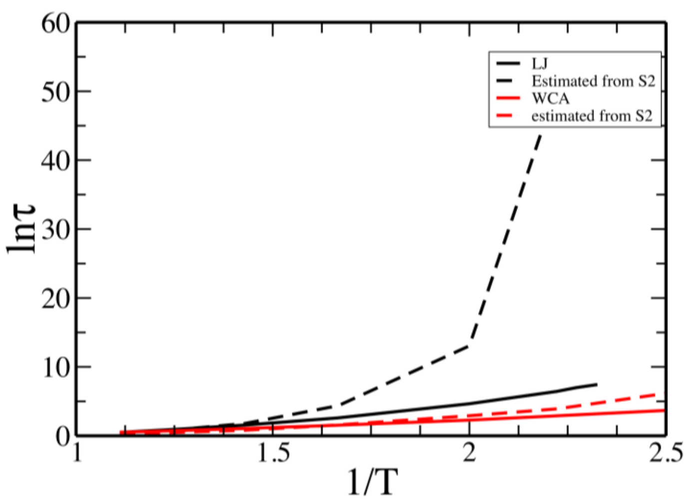
System	K_T	K_{T2}	K_{VFT}	K_{VFT2}
LJ	0.2980	0.7078	0.2026	0.3843
WCA	0.1892	0.3891	0.1648	0.2450

Pair correlation ➔ larger Kinetic and thermodynamic fragility

$$\frac{K_{VFT}^{LJ}}{K_{VFT}^{WCA}} = 1.23 \qquad \frac{K_{VFT2}^{LJ}}{K_{VFT2}^{WCA}} = 1.57 \qquad \frac{K_{T}^{LJ}}{K_{T}^{WCA}} = 1.575 \qquad \frac{K_{T2}^{LJ}}{K_{T2}^{WCA}} = 1.82$$

Pair correlation ➔ larger difference in fragility between the WCA and LJ system ➔ inconsistence with expectation

Contribution from many body entropy



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

$$\tau_{est}(T) = \tau_0(T)\exp\left(\frac{A}{TS_{C2}}\right)$$

$$S_C = S_{C2} + \Delta S$$

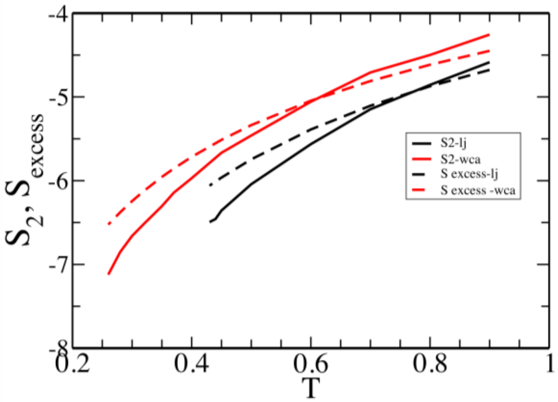
$$\ln\tau - \ln\tau_{est} = -A\frac{\Delta S}{TS_C S_{C2}}$$

Many body contribution more for LJ system larger effect on the relaxation time ➔ supports earlier finding

Many body contribution to entropy speeds up the dynamics ➔ inconsistence with expectation

Temperature evolution of RMPE (ΔS)

RMPE → effect of three body and higher order correlation
At high T → RMPE decreases the total entropy

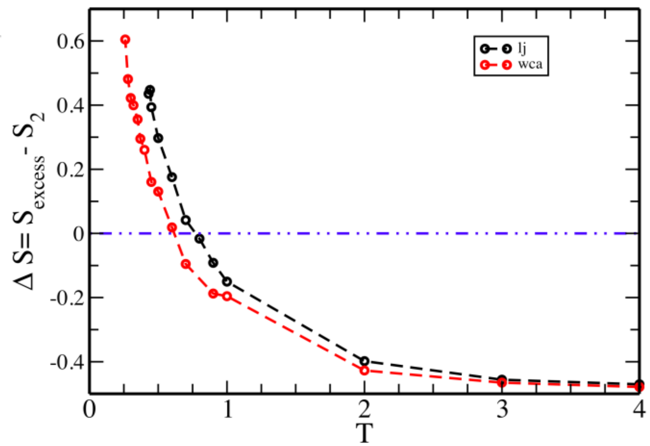


Crossover between S_{ex} and S_2

↓

RMPE crosses over from –ve to +ve

Liquid –Solid transition ΔS=0 connected to freezing

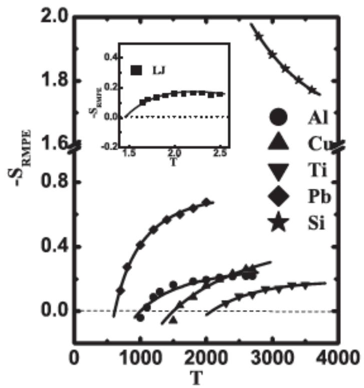


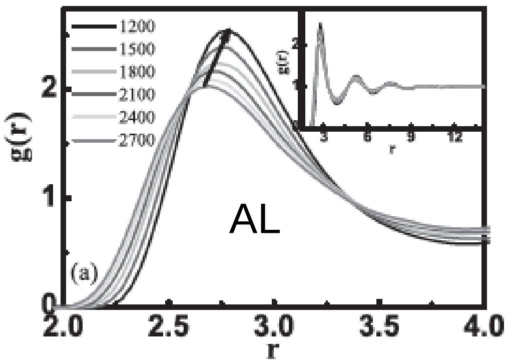
System	T(ΔS=0)
LJ	0.77
WCA	0.61

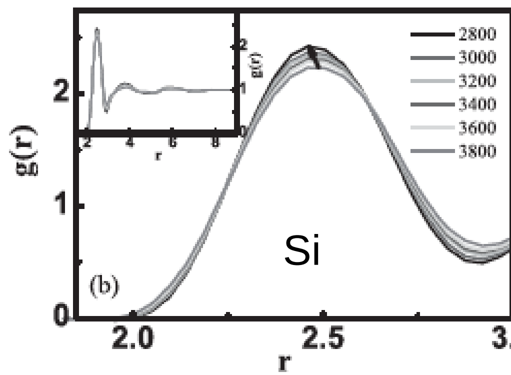
Increase in ordering → Increase in ΔS → weaker T dependence of entropy

Singh et. al. J. Chem Phys 137, 024508 (2012): Krekelbberg et. al. J. Chem Phys. 128, 161101 (2009)

Effect of Ordering on pair correlation







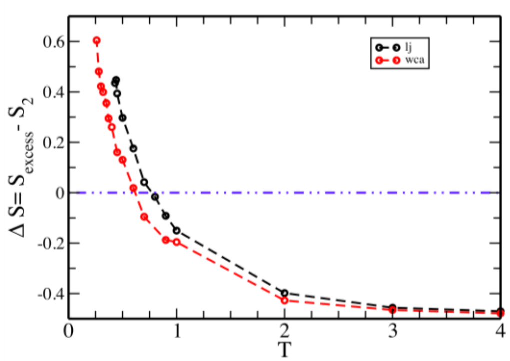
Cao et al. J. Chem. Phys. 134, 044508 (2011)

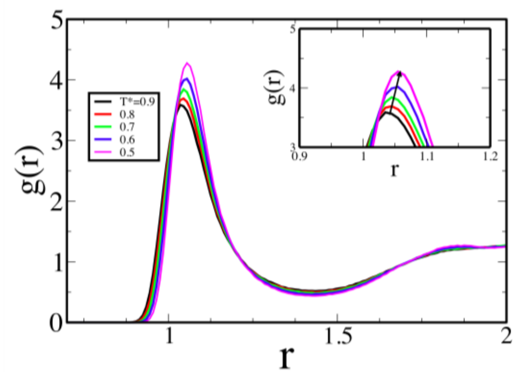
ΔS increasing ➔ peak position shift of g(r) to higher r

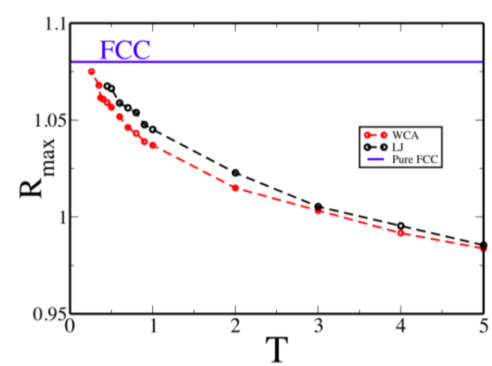
What kind of ordering ??

“A” particles in KA model shows tendency towards FCC ordering

Banerjee et al. J. Chem Phys. **139**, 104501 (2013): S. Toxvaerd et al. , J. Chem. Phys**.** **130,** 224501 (2009)**.**







Correlation between fragility and cooperativity

- Systems with growing $\Delta S \rightarrow$ negative correlation of fragility and cooperativity
- Systems with decreasing $\Delta S \rightarrow$ positive correlation of fragility and cooperativity

Consistent with previous studies

- Difference in dynamics → Thermodynamic in origin

Hocky, Markland and Reichman PRL,**108**, 225506 (2012)

- Pair correlation not enough to describe dynamics at low

Berthier & Tarjus, PRL **103**, 170601 (2009); PRE **82**, 031502 (2010); EPJE 34, 96 (2011) ; JCP 134, 214503 (2011)

- LJ system → larger contribution from many body correlation

Coslovich PRE **83**, 051505 (2011)

Surprises

- Pair correlation responsible for larger difference in dynamics between LJ and WCA
- Many body correlation → Residual multi particle entropy → reduces the difference between the dynamics

Thank You !