What can thermal fluctuations tell us about fragility?

Thomas B. Schrøder

Collaborators:
Ulf R.Pedersen
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Jon Papini
Nicholas Bailey
Jeppe C. Dyre

Fragility of Viscous Liquids: Cause(s) and Consequences, Copenhagen 2008

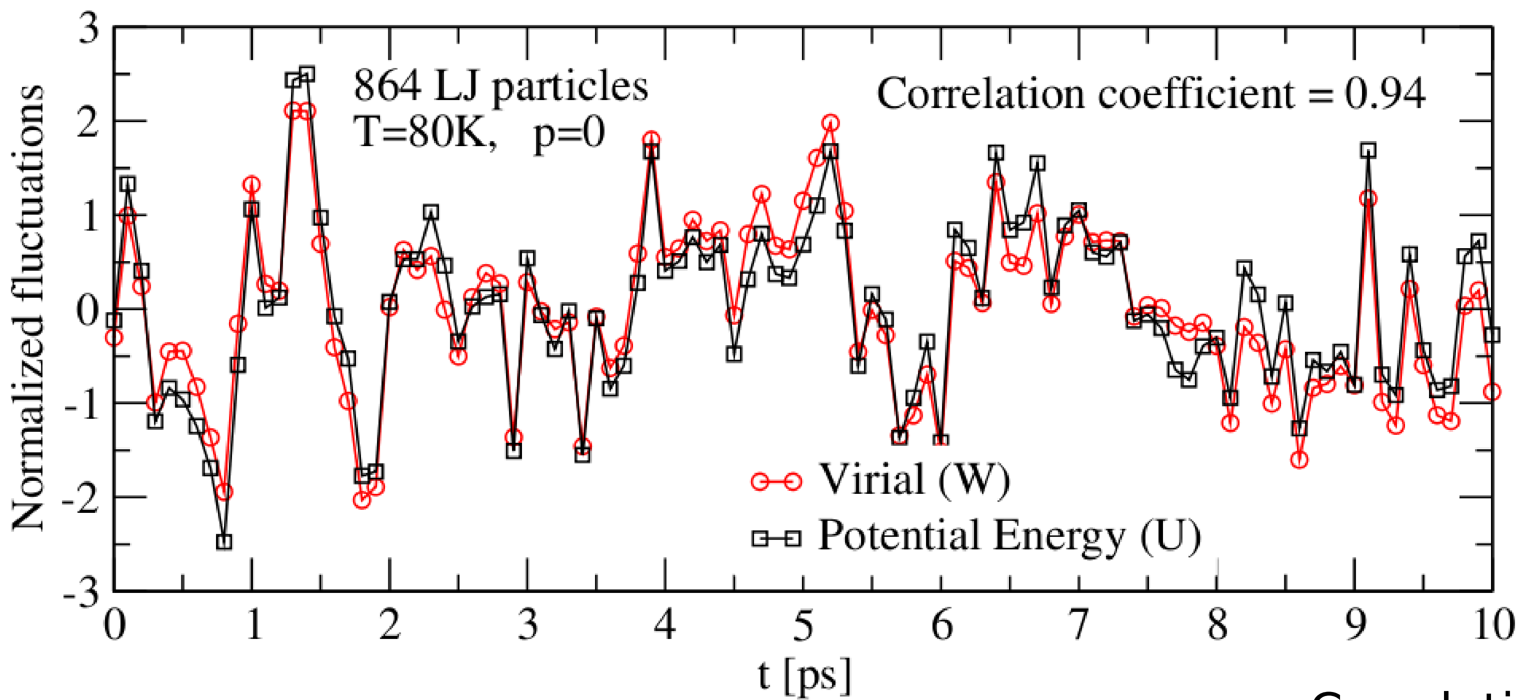
Glass and Time

The single component Lennard-Jones liquid revisited

- probably the most studied liquid in the history of computer simulations

Pressure and energy split in kinetic and configurational parts:

$$E(t) = K(t) + \underline{U(t)} \qquad p(t)V = Nk_B T(t) + \underline{W(t)}$$



$$U_{LJ} = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

MD simulations
NVT-ensemble

$$\Delta U(t) \equiv U(t) - \langle U \rangle$$

$$\Delta W(t) \equiv W(t) - \langle W \rangle$$

Correlation coefficient:

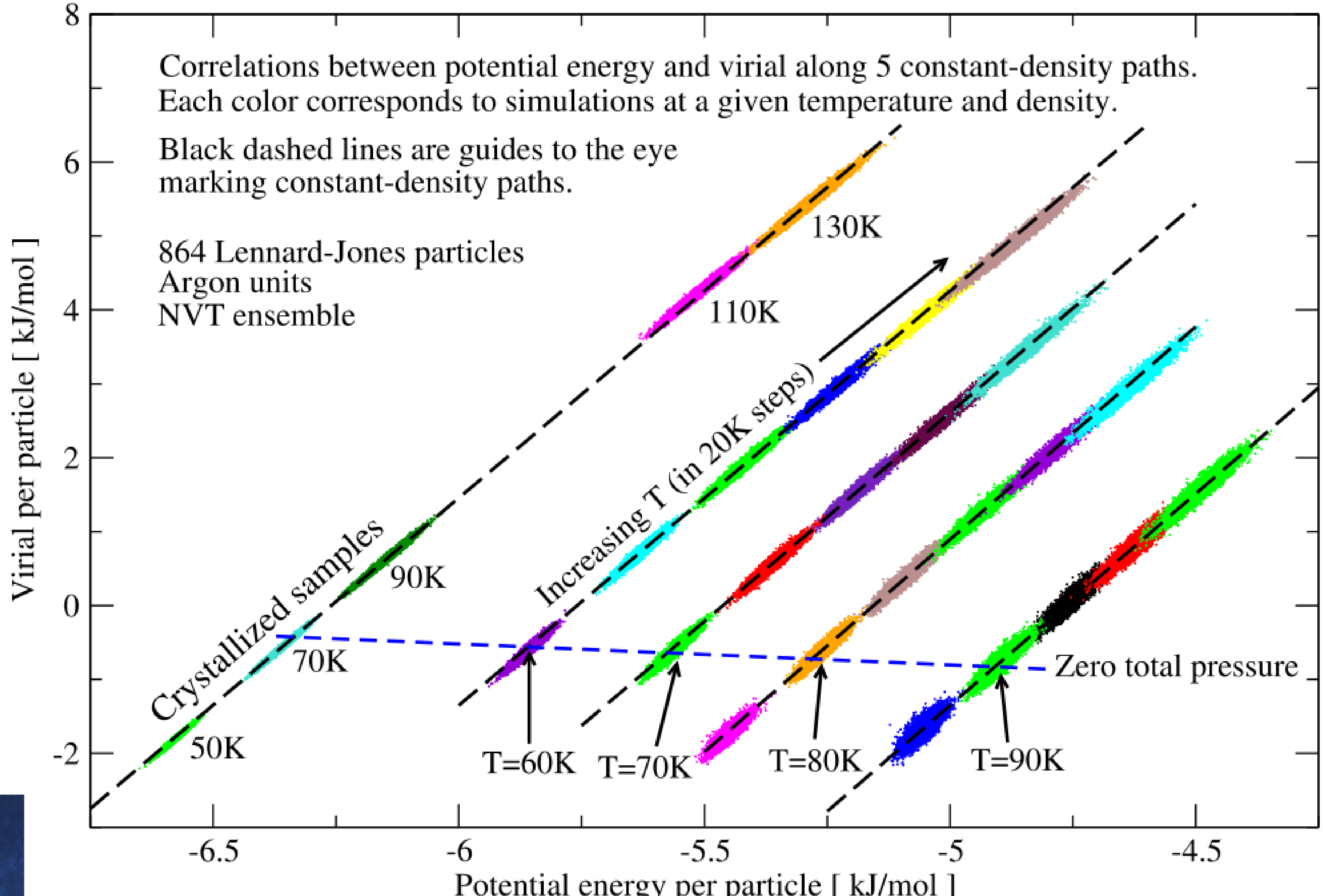
$$R \equiv \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}}$$

Conclusion:
W(t) and U(t) instantaneously correlated

[Pedersen et al. PRL 100 015701 2008]

Let's look at more state-points:

Each 'blob': scatter-plot of (W,U) over 10ns, after 10ns equilibration



R > 0.9 (Except for p<0)

Slopes: $\sqrt{\frac{\langle(\Delta W)^2\rangle}{\langle(\Delta U)^2\rangle}} \approx 6.0 \ (\pm 0.6)$

The explanation

Conjecture:
At a given state-point, the fluctuations are well described by an effective power-law:

$$U(r) = k r^{-n} + U_{.} \quad \Rightarrow$$

$$W \equiv -\frac{1}{3}\sum_{pairs} r\frac{\partial U}{\partial r} = \frac{n}{3}\left(U - U_0\right)$$

k, n and U_0 are allowed to depend (weakly) on state-point. At a given state-point:

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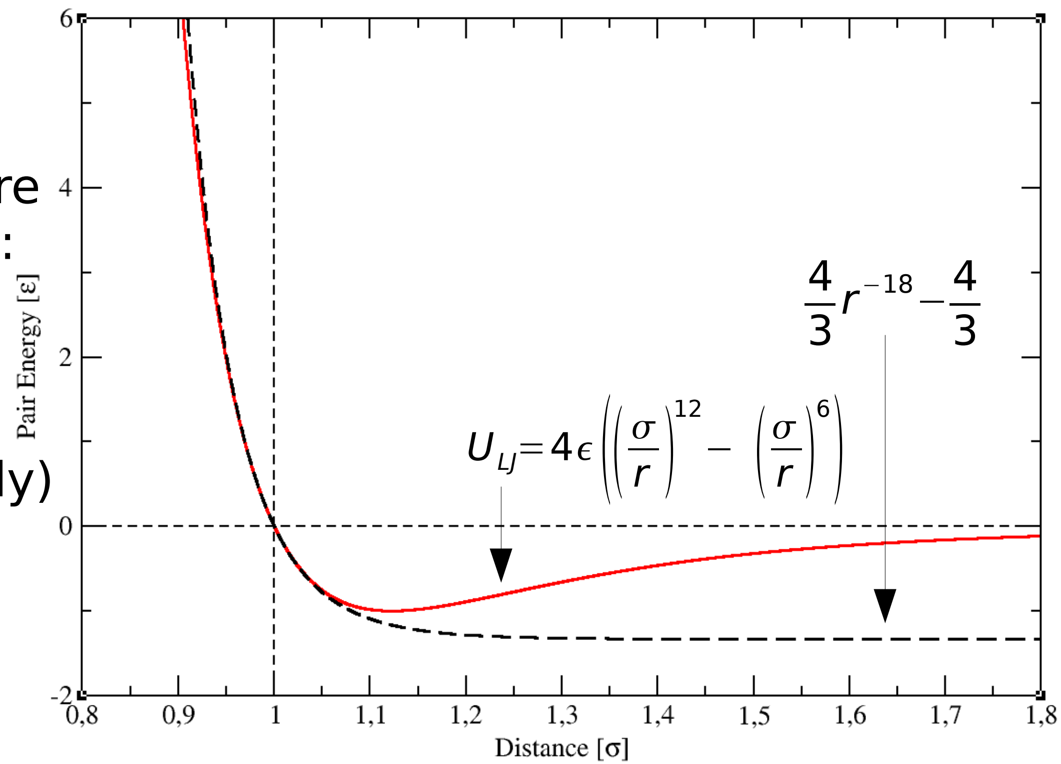
Remember: We are finding slopes ~ 6

The effective power-law



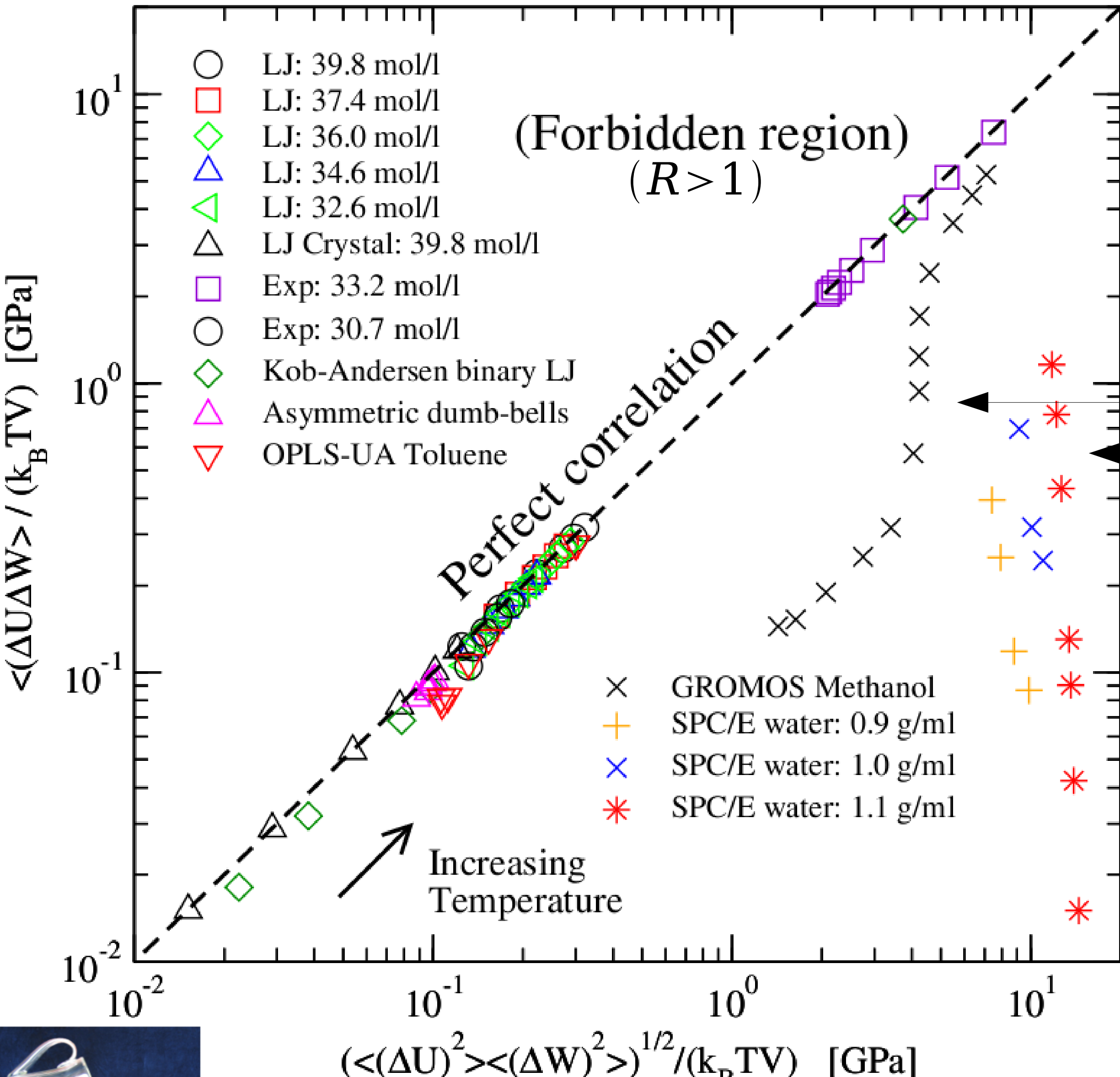
The more subtle explanation

$$U_{LJ}(r) = k r^{-n} + \underline{br} + U_0 + U_{rest}(r)$$

- Explanation confirmed directly by simulations
- Effective exponent weakly dependent on state point
- Experimental data for supercritical Argon: R=0.96

[N. Bailey et al. ArXiv:0807.055 (2008); to appear]

How general are the correlations?



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Competing interactions destroy the correlation:

$$U = U_{Coulomb} + U_{LJ}$$

$$W = W_{Coulomb} + W_{LJ}$$

Correlated

Correlated

Not correlated

- there exists a class of “strongly correlating liquids”

[Pedersen et al. PRL 100 015701 2008]

Properties of strongly correlating viscous liquids, I

- Defining property: $\Delta W(t) = \gamma \Delta U(t)$, 'slope' slightly dependent on state point
- $\Delta p(t) = \frac{\gamma}{V} \Delta E(t)$, on "long time-scales"

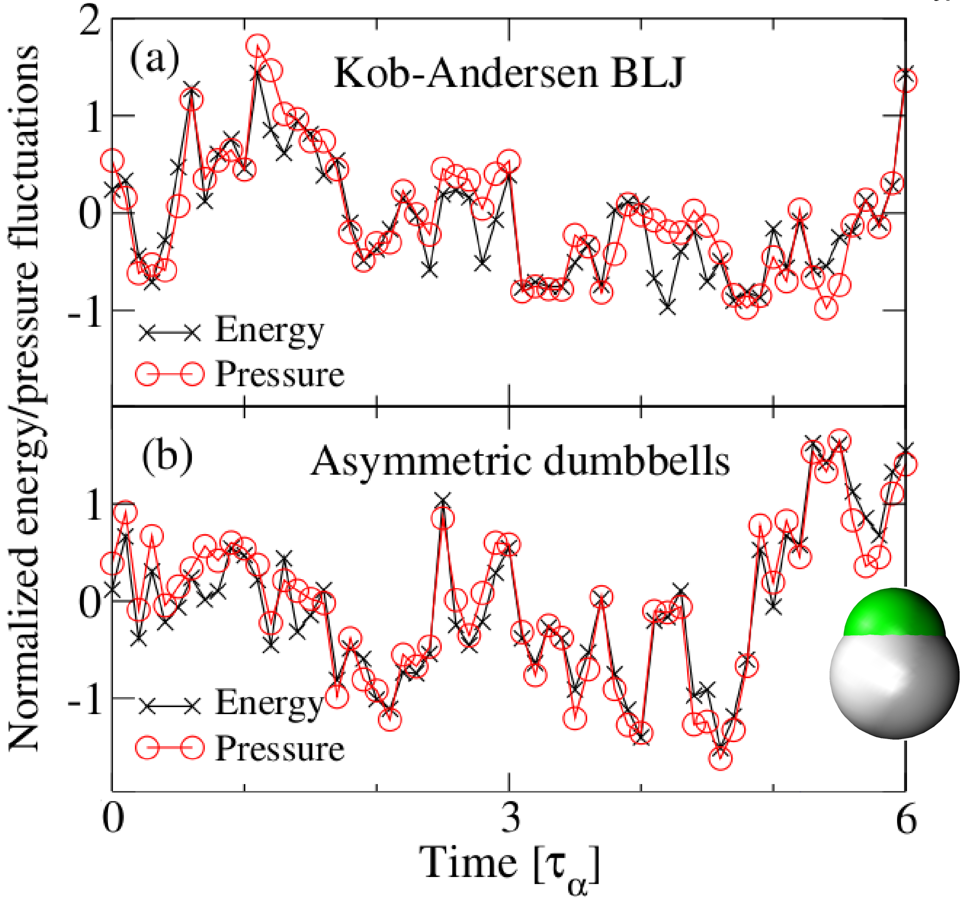
Data averaged over $0.1\tau_\alpha$ $\qquad \tau_\alpha \approx 1\, ns$

$$p(t)V = Nk_B T(t) + W(t)$$

$$E(t) = K(t) + U(t)$$

+

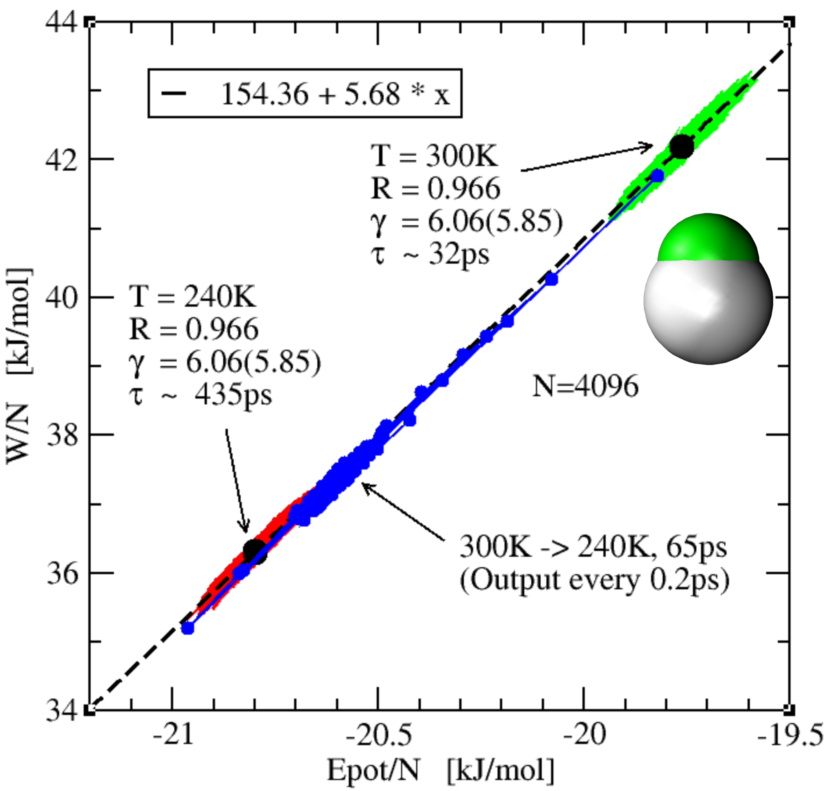
Seperation of time-scales

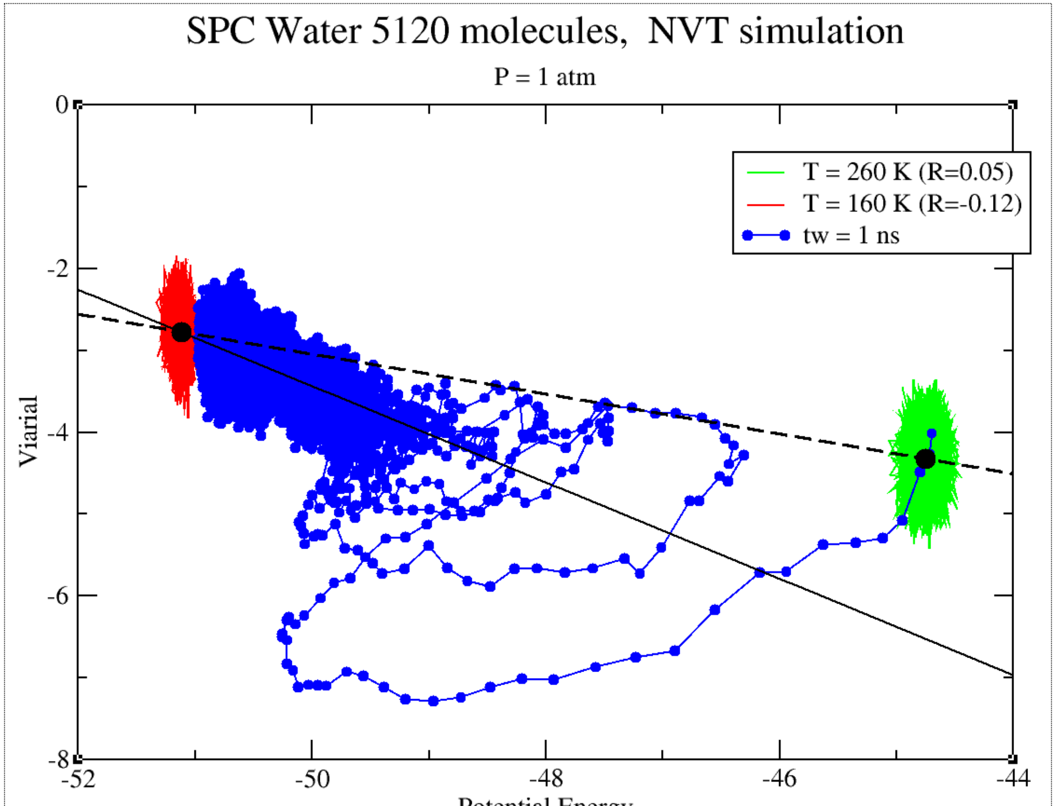


[Pedersen et al. PRE 77 011201 2008]

Properties of strongly correlating viscous liquids, II

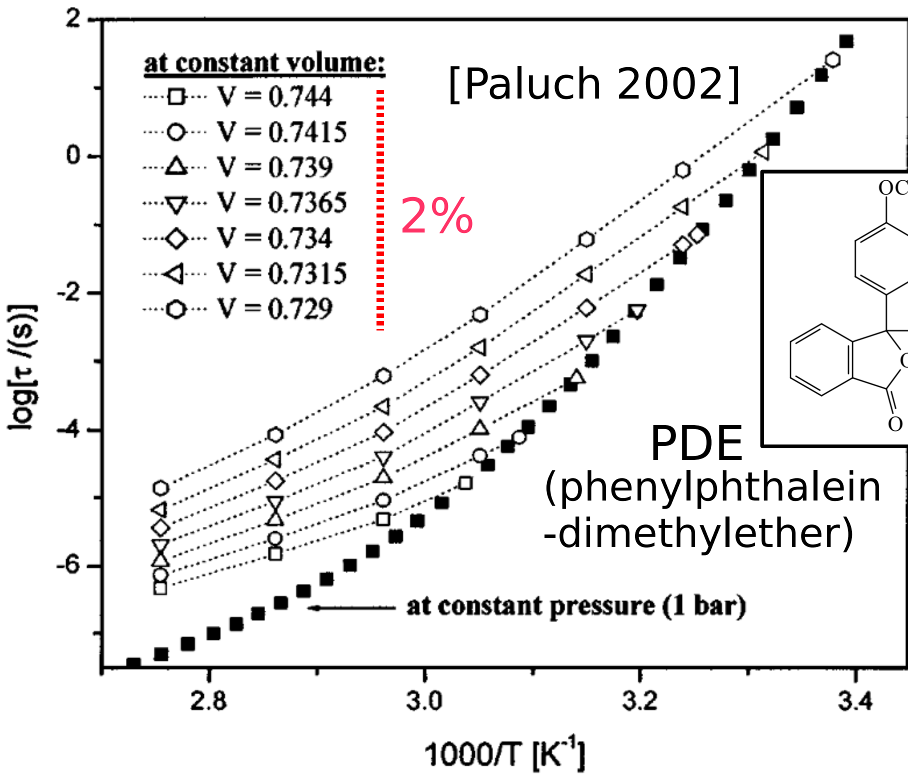
- Defining property: $\Delta W(t) = \gamma \Delta U(t)$, 'slope' slightly dependent on state point
- $\Delta p(t) = \frac{\gamma}{V} \Delta E(t)$, on "long time-scales"
- Fluctuation Dissipation theorem: $-Tc_V''(\omega) = \gamma^2 K_T''(\omega) = -\gamma T \beta_V''(\omega)$
  Three 'independent' thermoviscoelastic response functions are proportional.
  [Ellegaard et al., JCP 126, 074502 (2007); Pedersen et al., PRE 77, 011201 (2008)]
- Single-parameter aging: $W(t) = \gamma U(t) + W_0$ even out of equilibrium (isochoric!)





Density scaling

[Paluch 2002]



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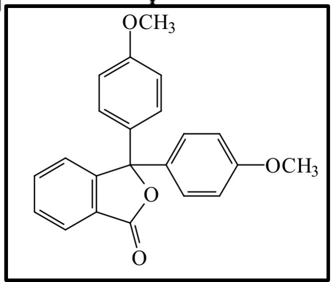
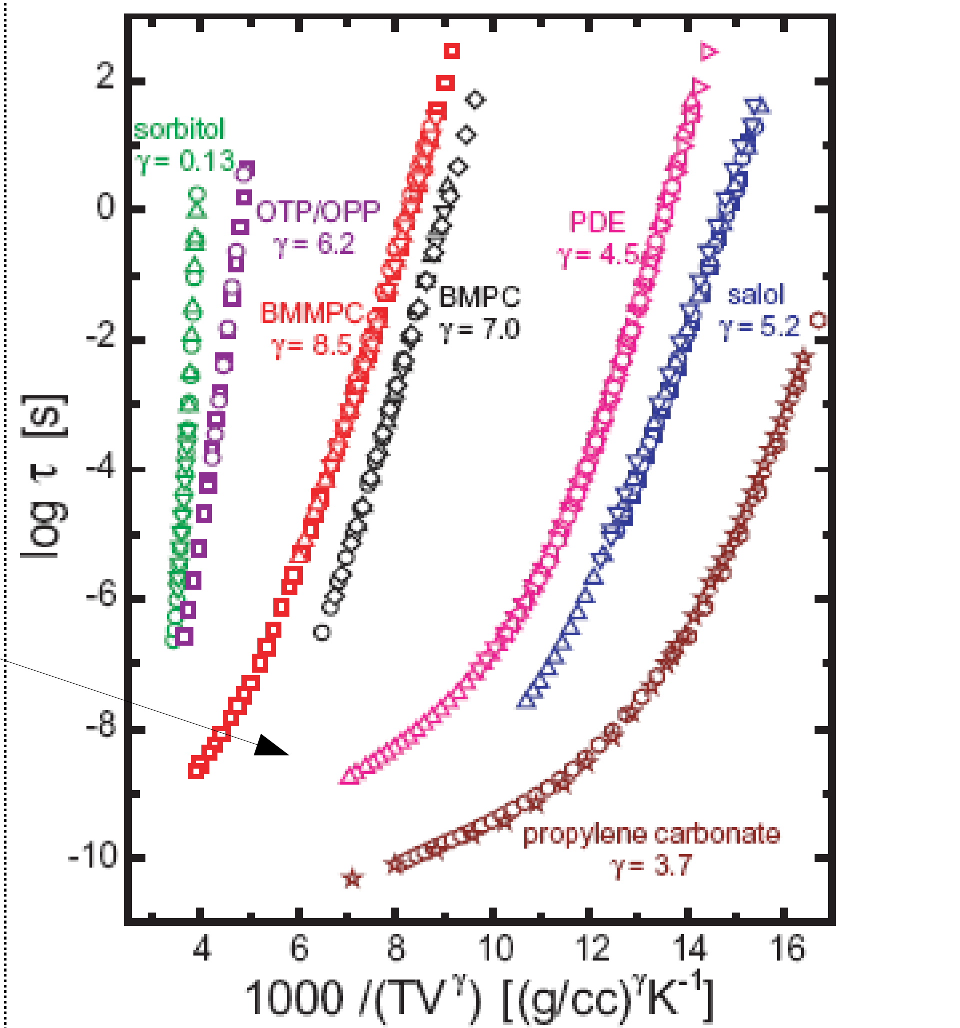


PDE
(phenylphthalein
-dimethylether)

[Roland et al., Rep. Prog. Phys., 2005]:



$$\tau = F(\rho^{\gamma}/T)$$

But: Is it the right form of scaling?
What is the explanation?
Does not work for all viscous liquids

Density scaling: $\tau = F(\rho^\gamma / T)$

Suggested explanation: Effective power-law

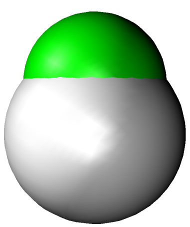
See eg. [Coslovich & Roland, JPC 2008]

Conjectures:

- Density scaling if (and only if) strongly correlating liquid.
- "Density scaling exponent" = "fluctuation exponent"

[Schrøder et al. ArXiv:0803.2199 (2008)]

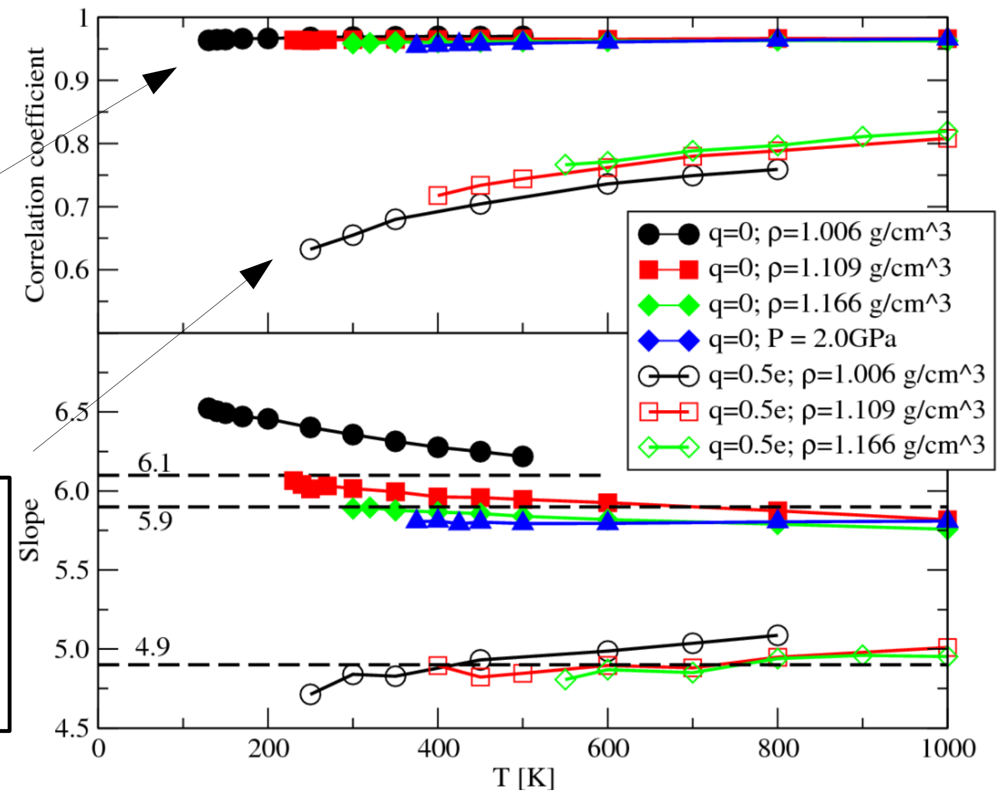
Asymmetric dumbbell:



Rigid bonds, Charges $\pm q$:

$q=0$:
Zero dipole moment
-> strongly correlating

$q=0.5e$:
Strong dipole moment
(20 x toluene, 4 x water)
-> NOT strongly correlating



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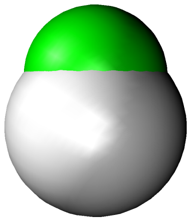

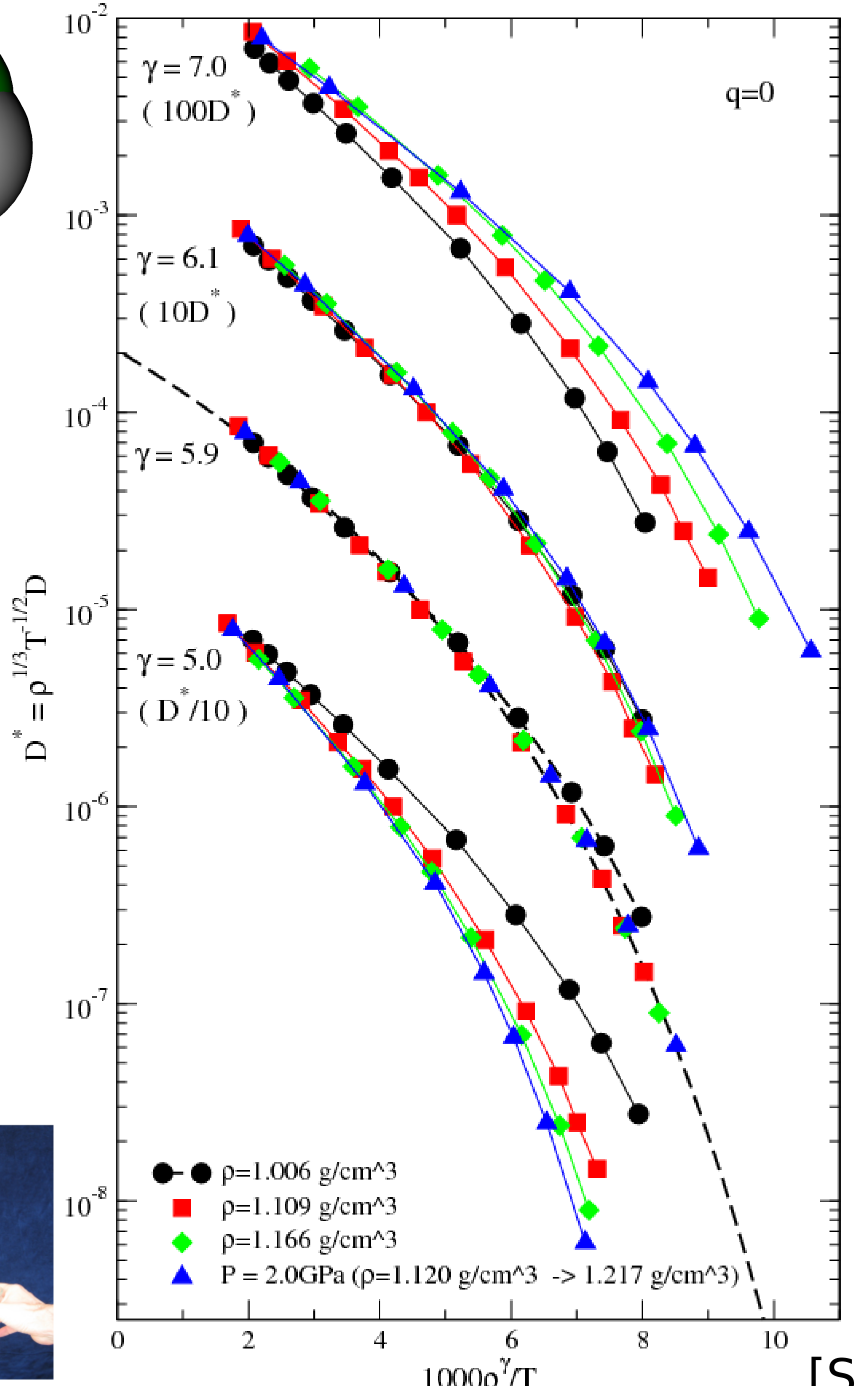

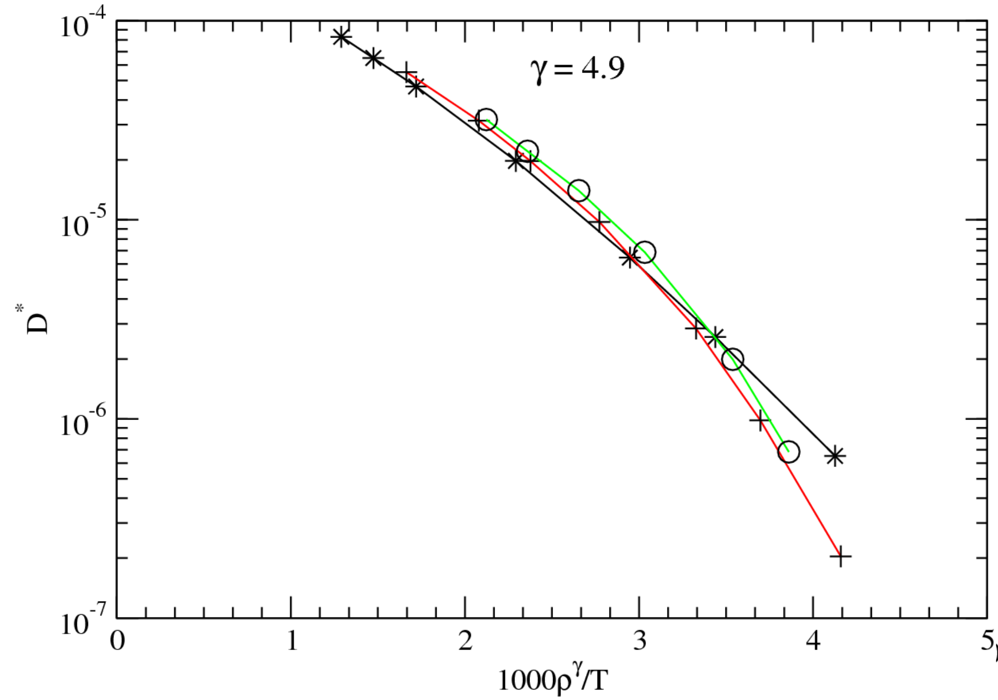

Conclusions:
- Density scaling works (q=0)
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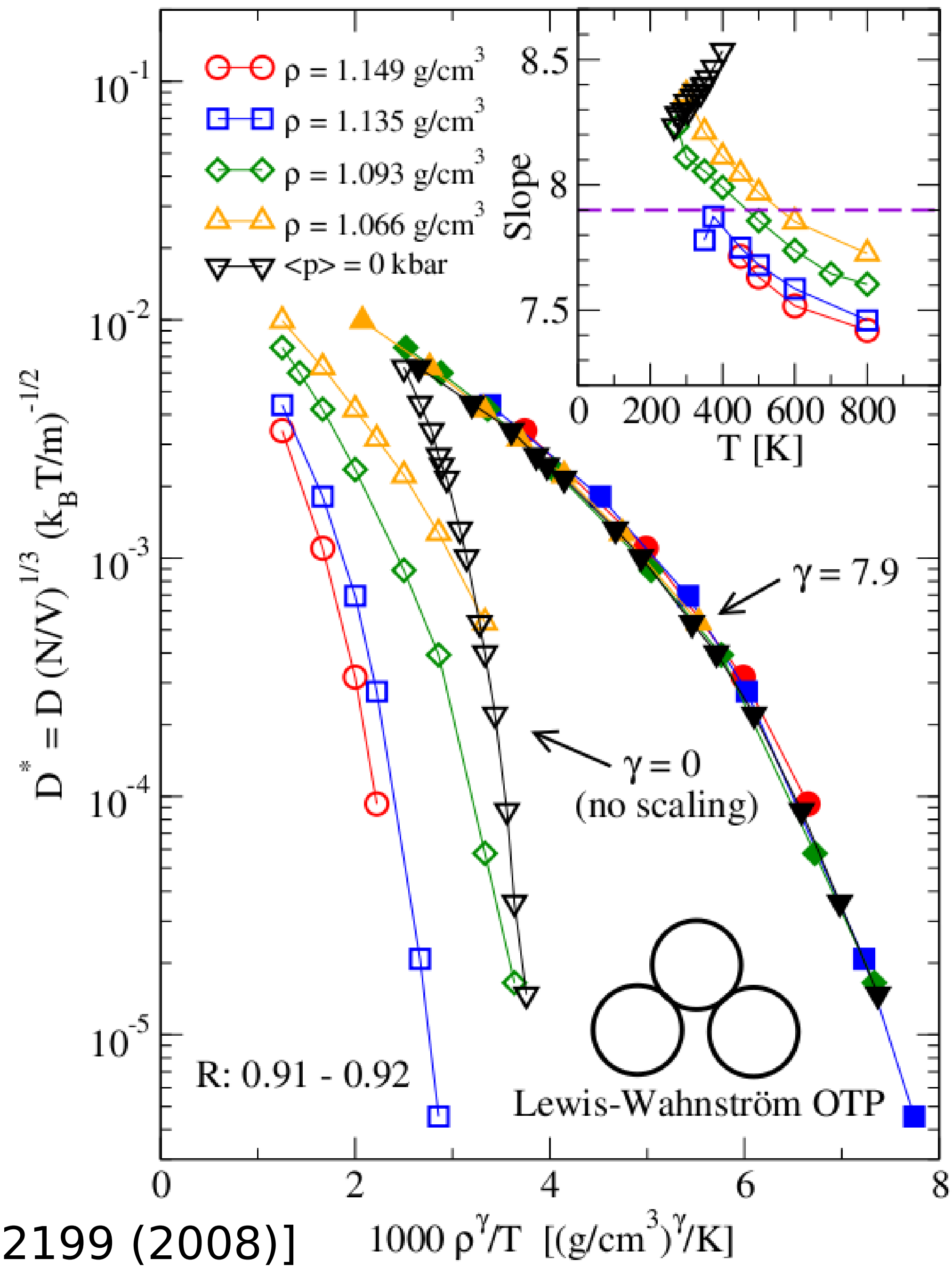
Density scaling in LW-OTP



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- Fragility: $m_P = m_\rho (1 + \alpha_P T_g \gamma)$ [K. Niss yesterday]

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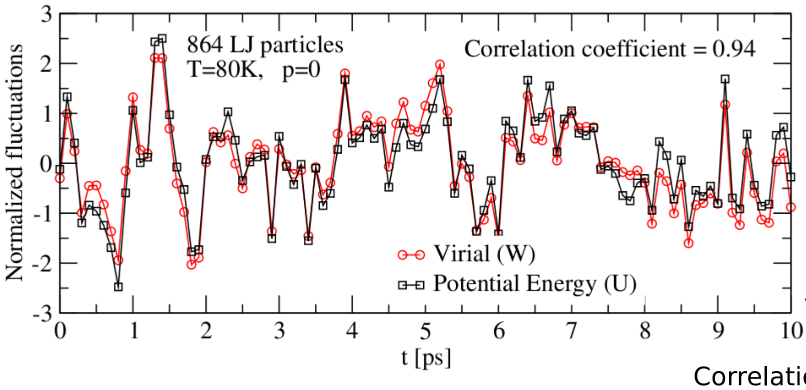

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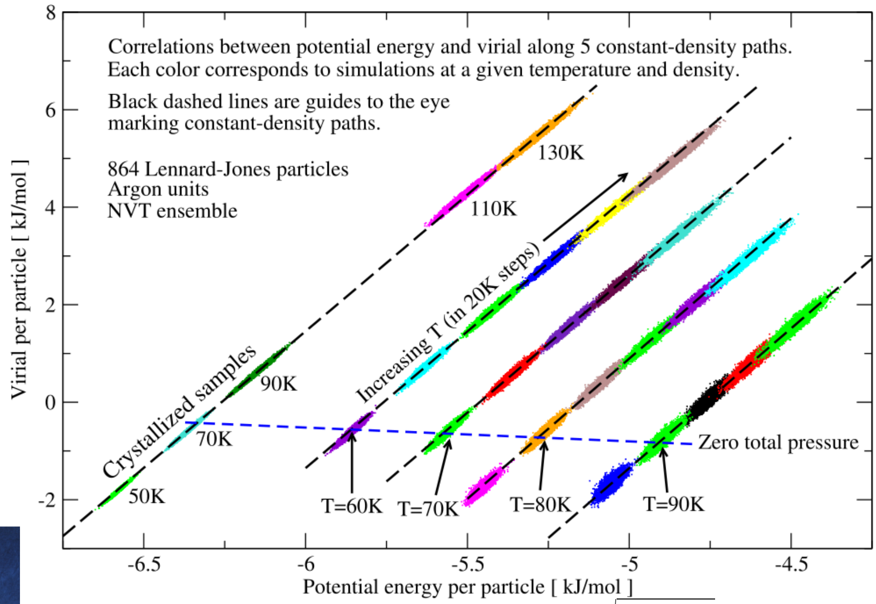

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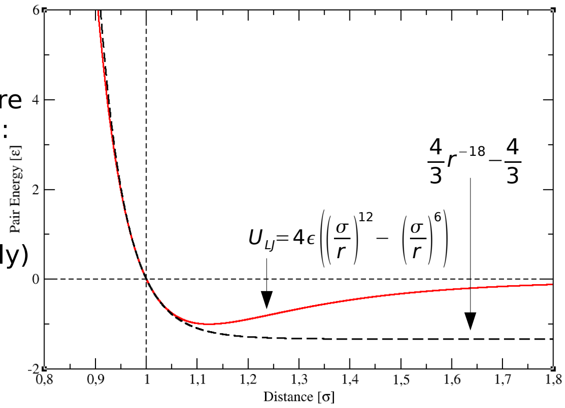

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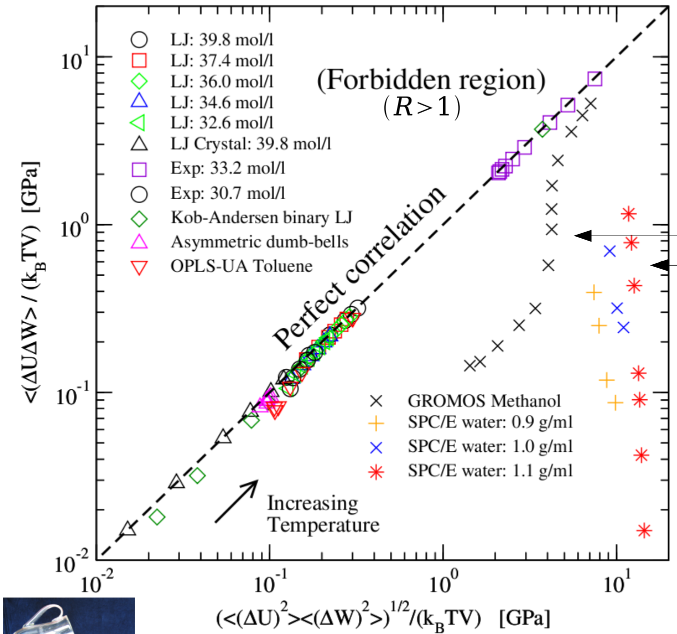

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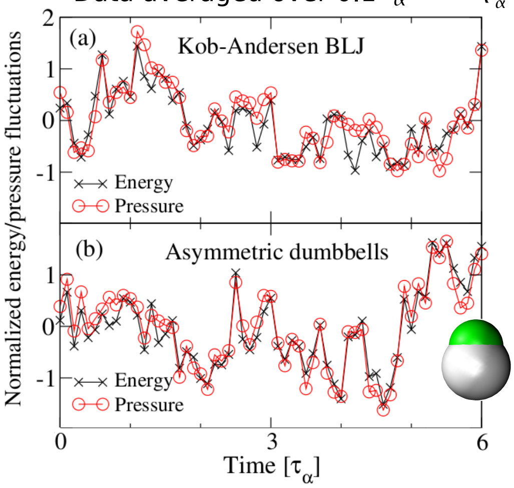

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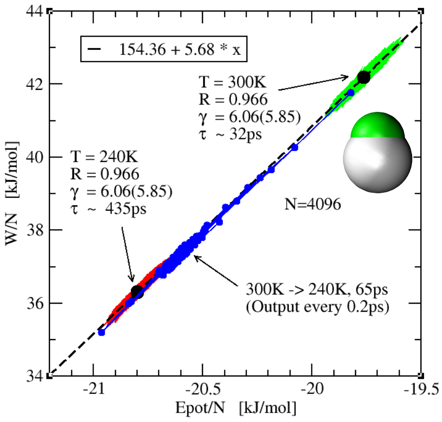
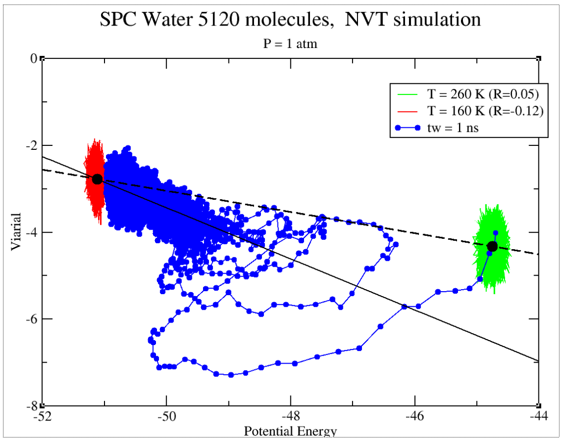
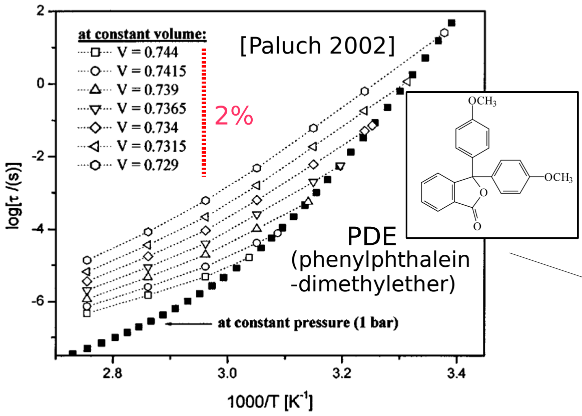




Density scaling



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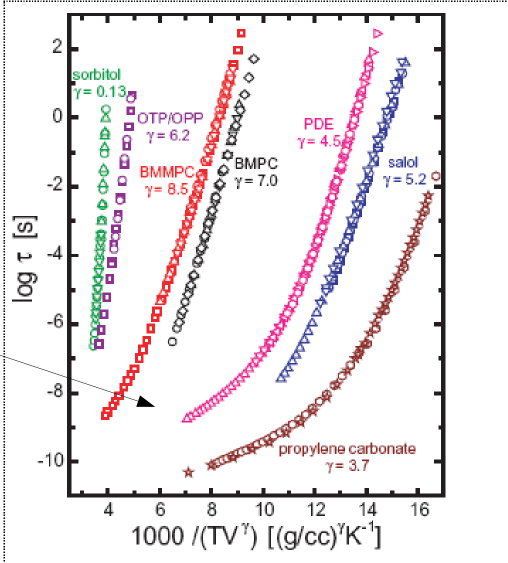

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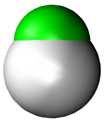

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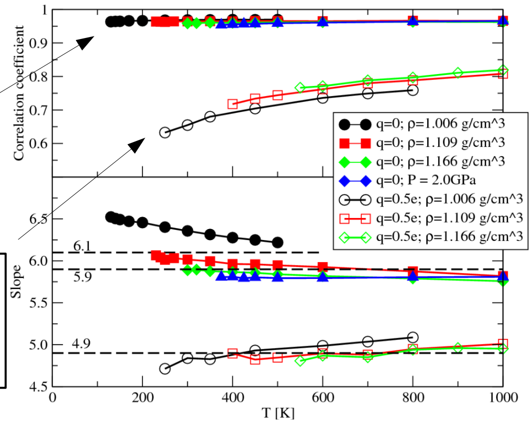

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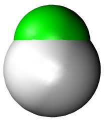

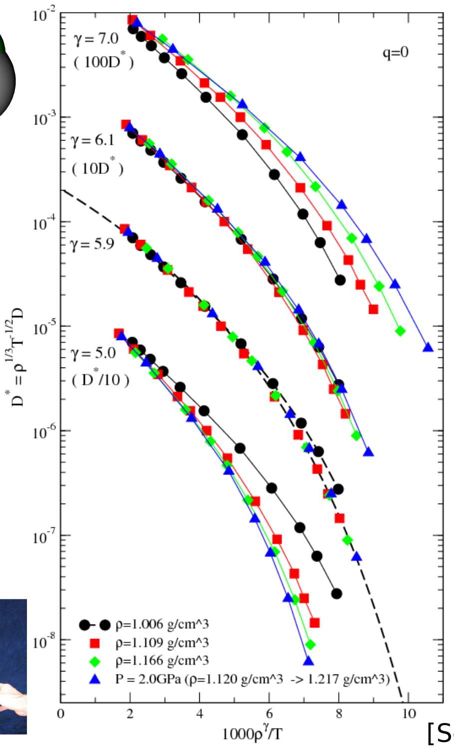

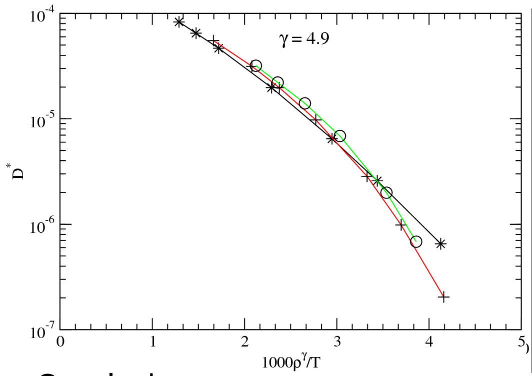

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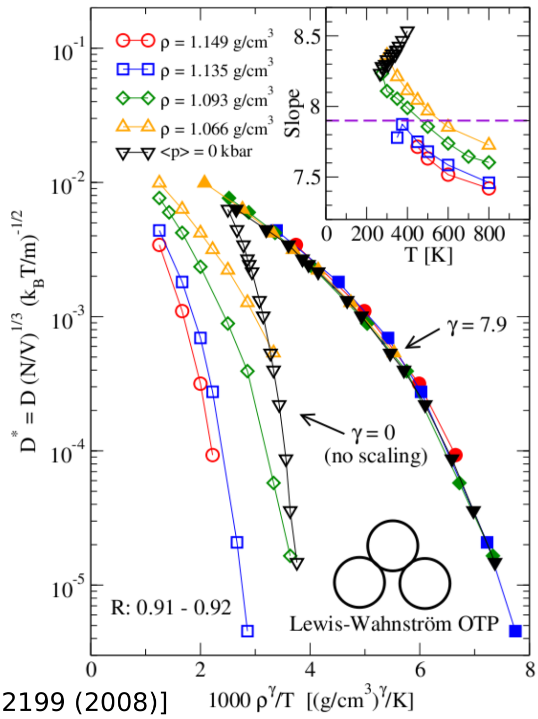

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