

Systems with hidden scale invariance: An overview of the isomorph theory. I

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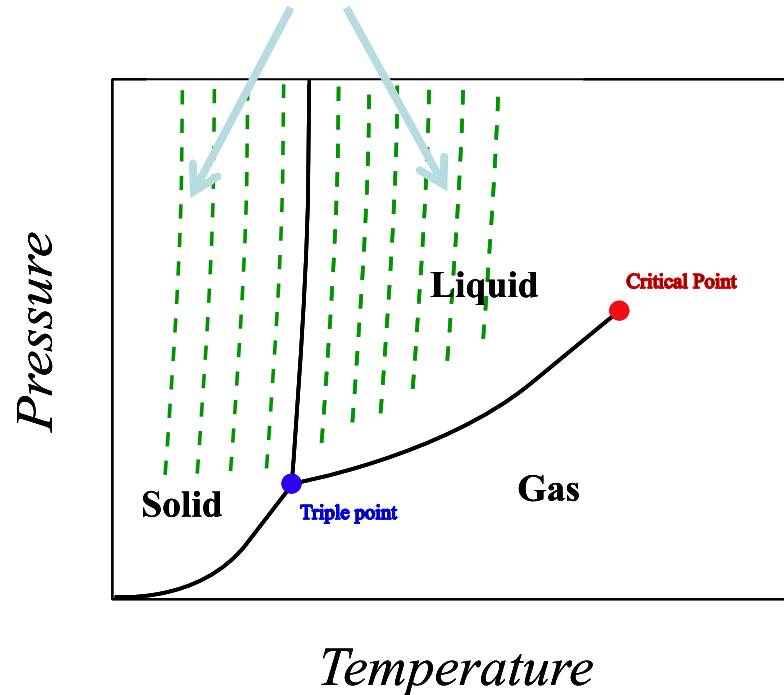
From Supercooled Liquids to Glasses: Current Challenges for Amorphous Materials
Beijing August 7-18, 2017

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Main idea

Isomorphs: Lines of invariant structure and dynamics



R-simple systems:

- van der Waals bonded
- metals
- weakly ionic/dipolar

Complex systems:

- hydrogen bonded
- covalently bonded
- strongly ionic/dipolar

Computing at *Glass and Time*

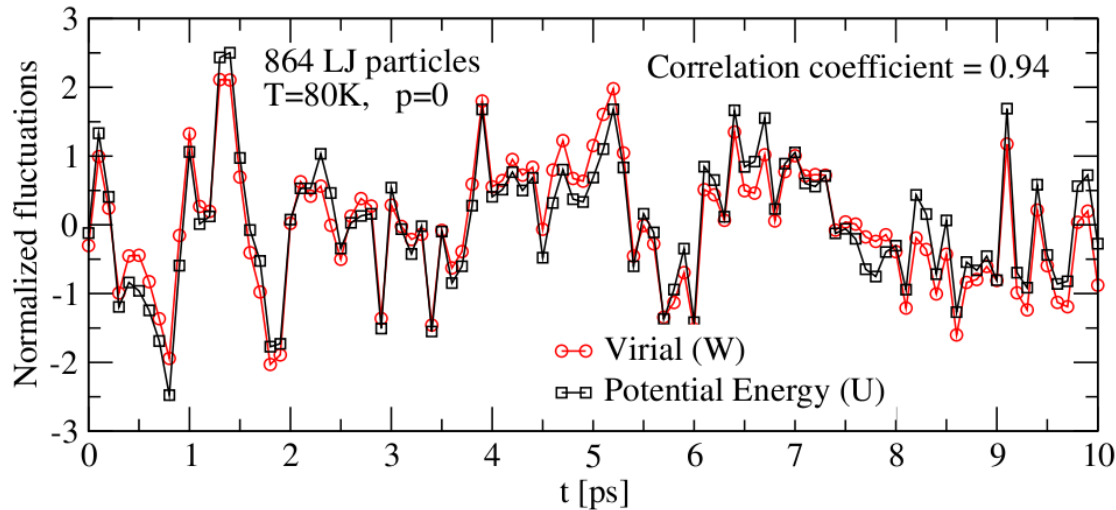


Computer clusters:

- 30 node standard cluster with dual cores (2005; upgraded 2014)
- An NVIDIA supercomputer with 92 GPUs, total theoretical peak performance: 85 TeraFLOPS (2008-...)
- Upgraded 2013 to 400 TeraFLOPS
- GPU software available at: <http://rumd.org> [arXiv:1506.05094]



Pressure-energy correlations



Lennard-Jones:

$$v(r)/\varepsilon = 4[(r/\sigma)^{-12} - (r/\sigma)^{-6}]$$

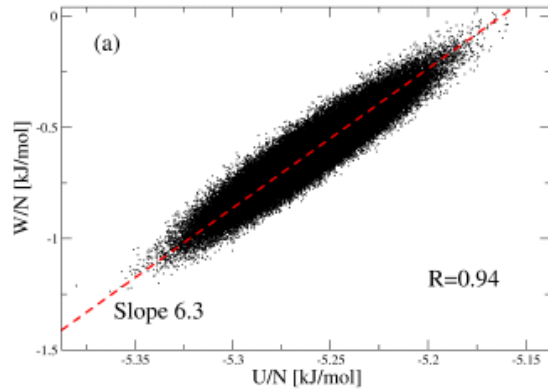
Virial W and potential energy U in LJ liquid (NVT ensemble)
[Phys. Rev. Lett. **100**, 015701 (2008)].

$$pV = Nk_B T + W$$

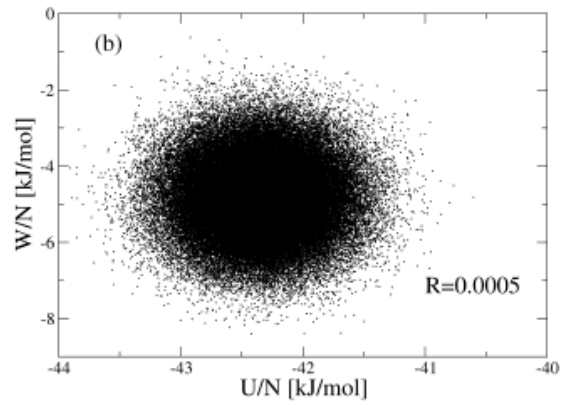
$$E = K + U$$



Scatter plots



Lennard-Jones liquid



TIP5P water



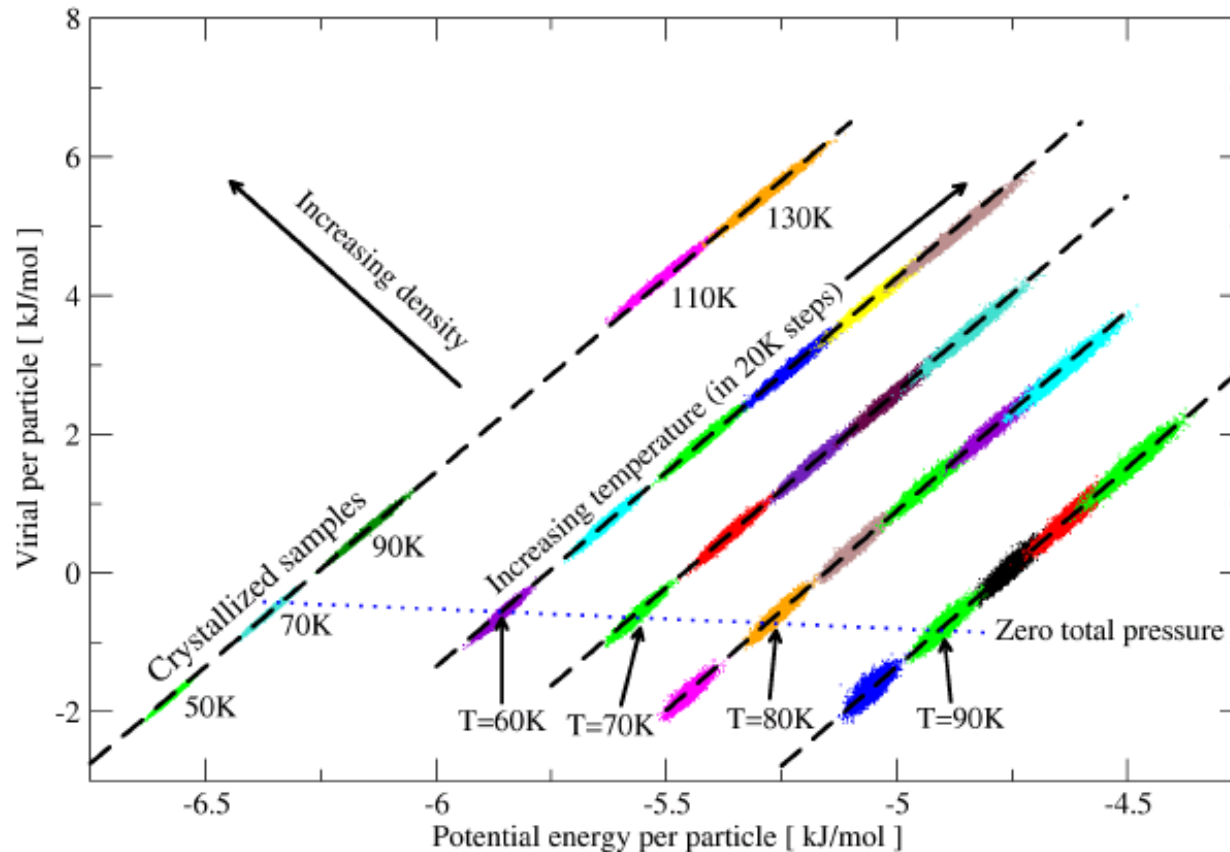
A useful number

The correlation coefficient:

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



Lennard-Jones liquid: A closer look

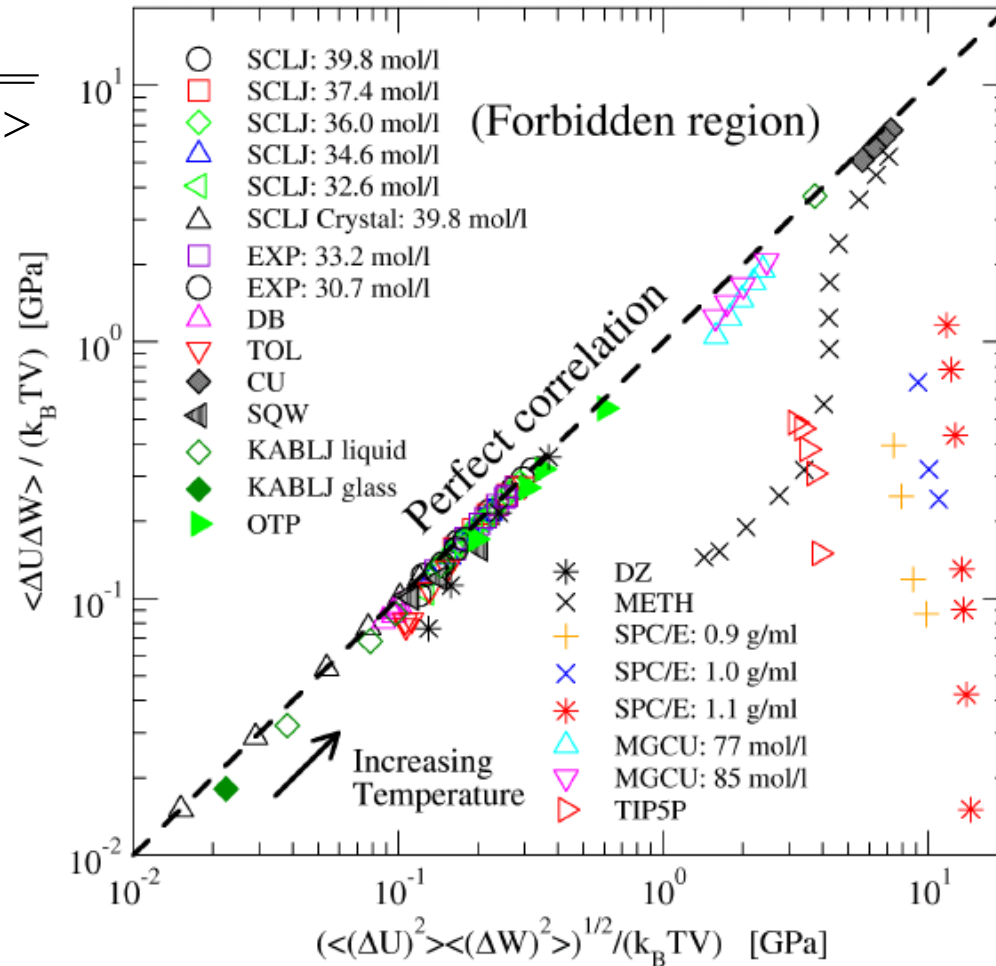


[Phys. Rev. Lett. **100**, 015701 (2008)].

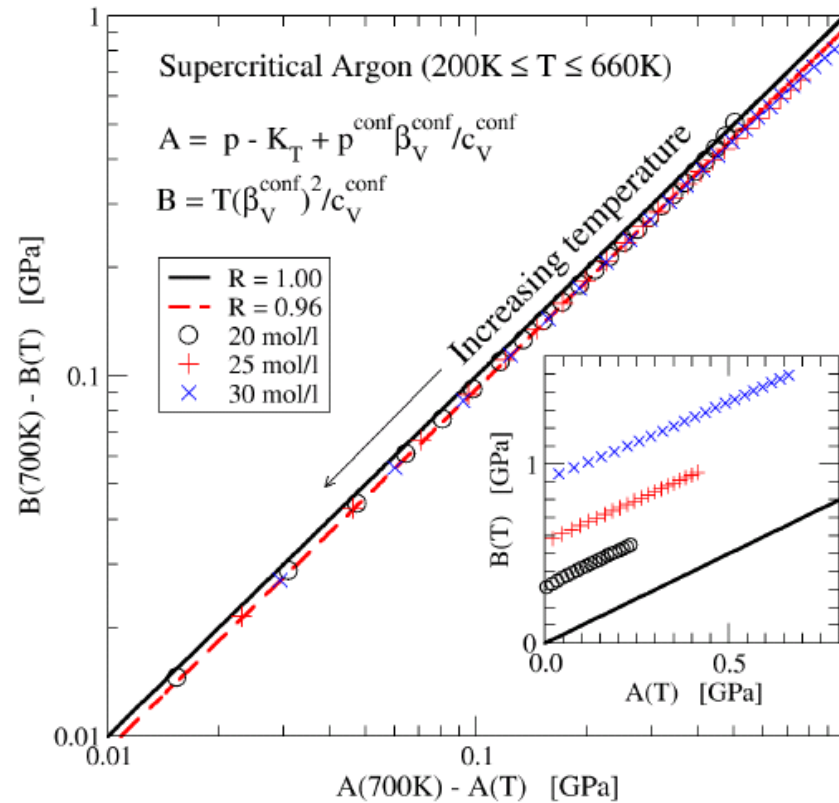


Other systems

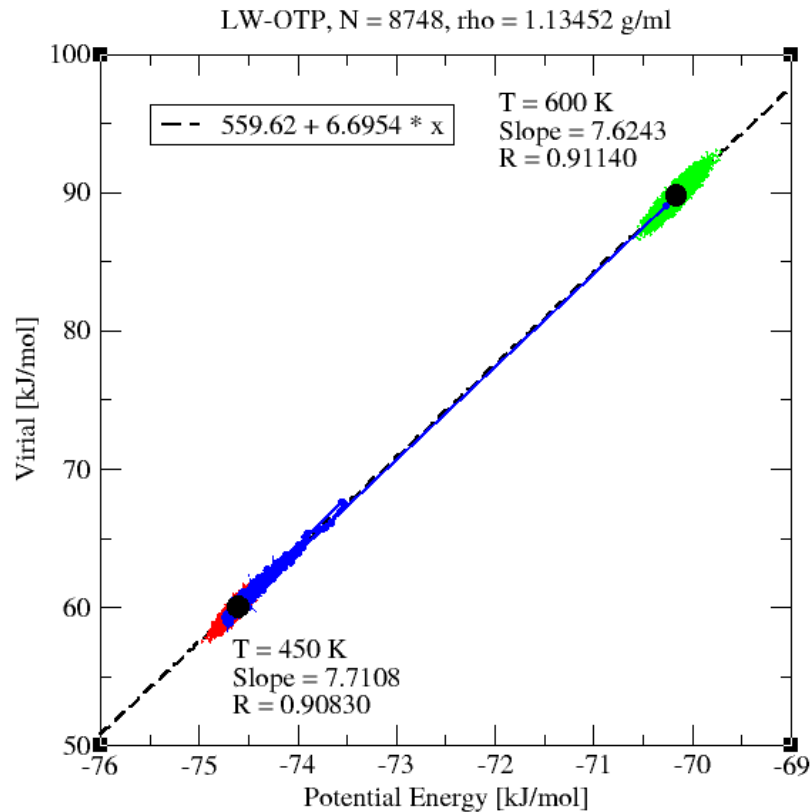
$$R = \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}}$$



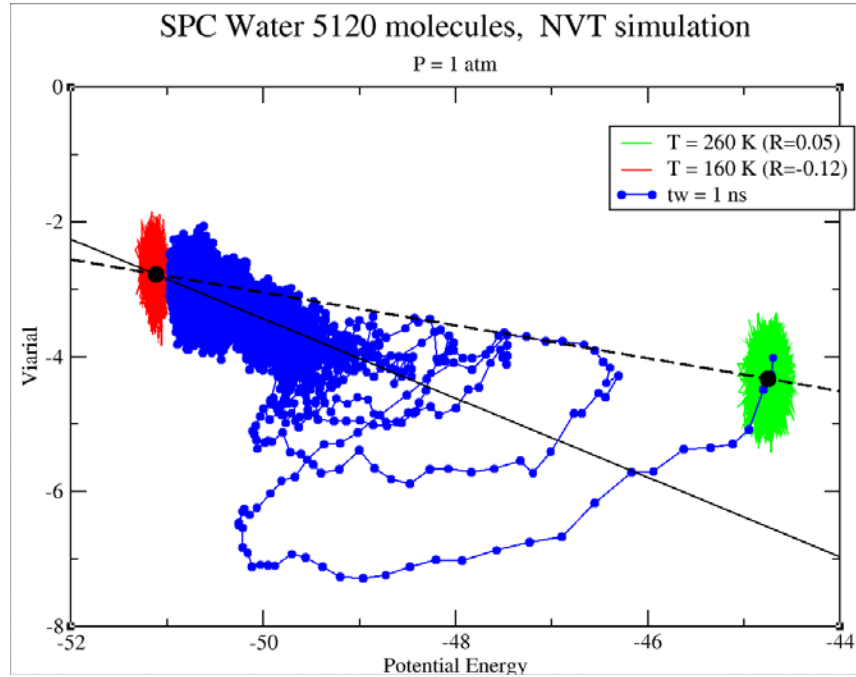
Supercritical Argon: 96% correlation



Aging: Orthoterphenyl (OTP)



Aging: Water



What causes the strong correlations?

Virial definition: $W = -\frac{1}{3} \sum_{ij} r_{ij} v'(r_{ij})$ $\Delta W(t) \cong \gamma \Delta U(t)$

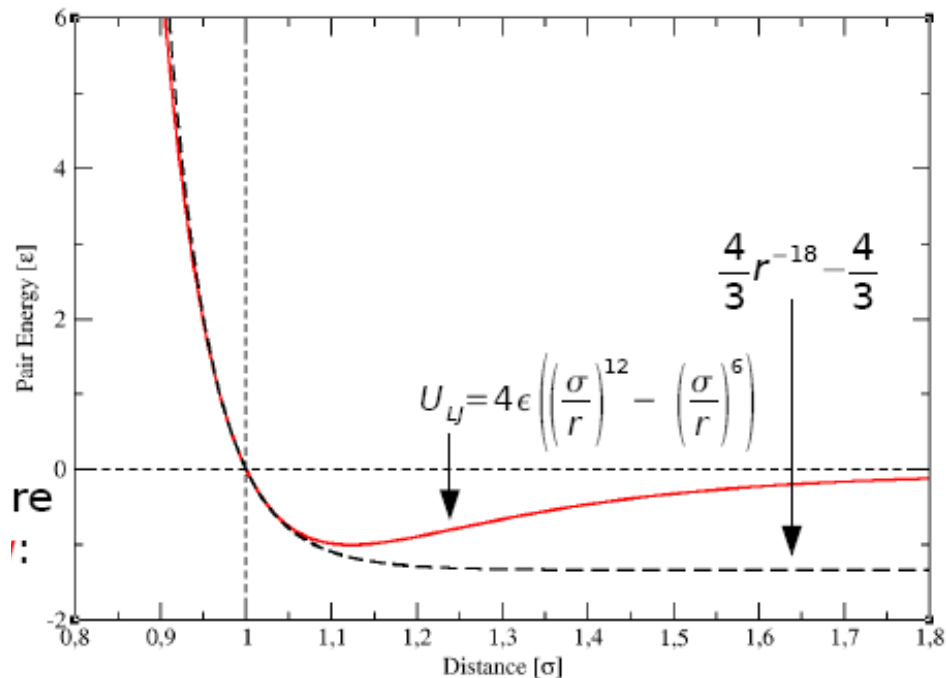
$v \propto r^{-n}$ implies $\gamma = \frac{n}{3}$

This suggests that $\gamma=4$ for the LJ system...



Lennard-Jones potential

The effective power-law



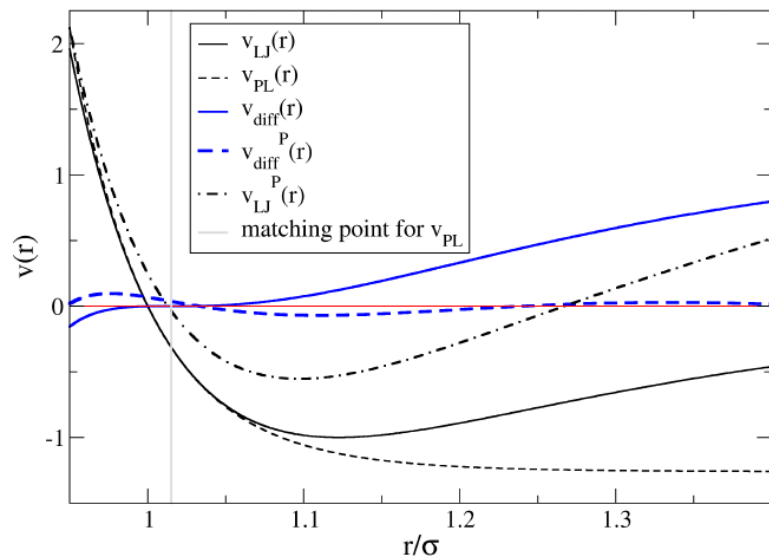
[see also Ben-Amotz and Stell, J. Chem. Phys. **119**, 10777 (2003)]



Origin of the hidden scale invariance of strongly correlating liquids: The "extended inverse power-law" (eIPL) potential

Strong virial / potential energy correlations are present whenever the potential can be fitted well around first structure peak by

$$v_{LJ}(r) \simeq Ar^{-n} + B + Cr$$



Fluctuations are almost not affected by the r-term; thus IPL approximation applies.

For details: JCP **129**, 184508 (2008);
JCP **131**, 234503 (2009).



Isomorph definition, v1 (2009)

$$\tilde{\mathbf{r}}_i \equiv \rho^{1/3} \mathbf{r}_i. \quad (4)$$

Two state points (1) and (2) with temperatures T_1 and T_2 and densities ρ_1 and ρ_2 are by definition *isomorphic* if they obey the following: Any two physically relevant configurations⁴³ of state points (1) and (2), $(\mathbf{r}_1^{(1)}, \dots, \mathbf{r}_N^{(1)})$ and $(\mathbf{r}_1^{(2)}, \dots, \mathbf{r}_N^{(2)})$, with same reduced coordinates have proportional NVT Boltzmann statistical weights:

$$e^{-U(\mathbf{r}_1^{(1)}, \dots, \mathbf{r}_N^{(1)})/k_B T_1} = C_{12} e^{-U(\mathbf{r}_1^{(2)}, \dots, \mathbf{r}_N^{(2)})/k_B T_2}. \quad (5)$$

[JCP **131**, 234504 (2009)]

Trivial example:

For inverse power-law (IPL) liquids, states with same are isomorphic (with $C_{12}=1$).

Physical content:

Same potential energy landscape (in temperature scaled units)

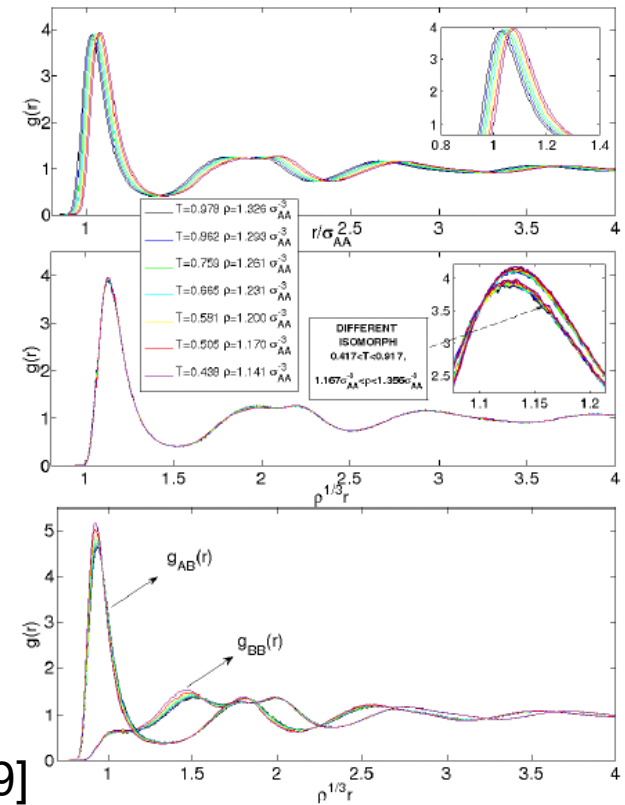
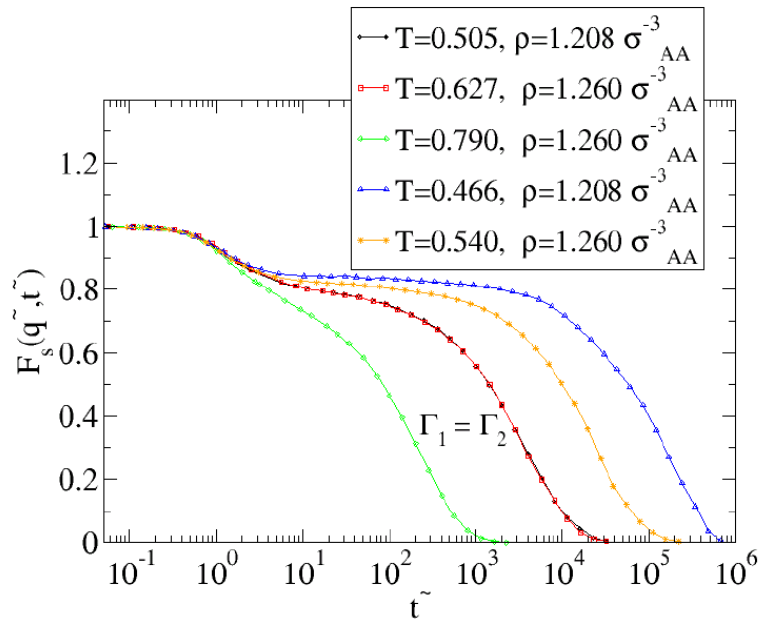


Isomorph properties

- 1) Isomorph state points have same excess (configurational) entropy.
- 2) Isomorph state points have same (scaled) relaxation time.
- 3) Isomorph state points have same (scaled) dynamics.
- 4) Isomorph state points have same (scaled) static equilibrium distributions.
- 5) Isomorph state points have same ...
- 6) Instantaneous equilibration for jumps between isomorph state points.
- 7) A liquid has isomorphs (to a good approximation) if and only if the liquid has strong correlations between equilibrium fluctuations of virial and potential energy.



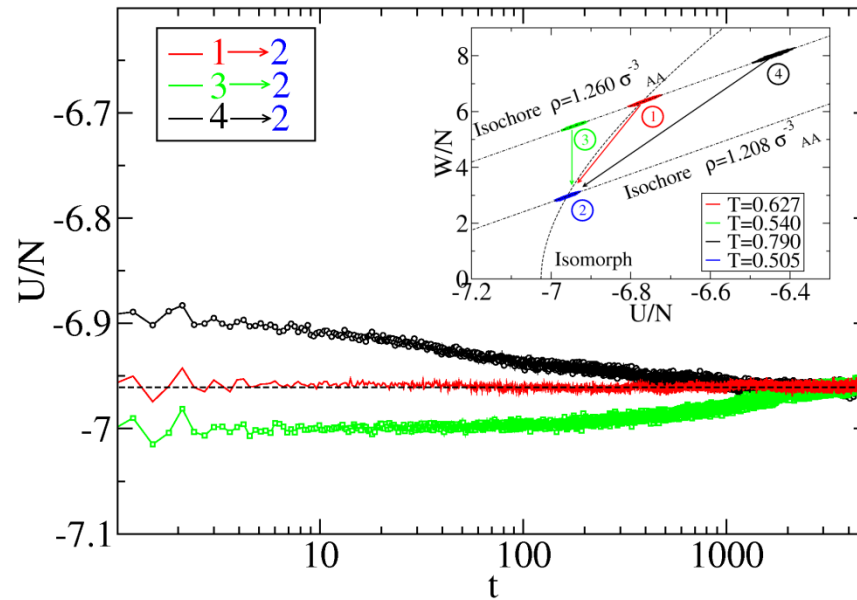
Results from computer simulations



[Kob-Andersen binary Lennard-Jones liquid, 2009]



Isomorphs jump (red)



[Kob-Andersen binary Lennard-Jones liquid, 2009]



”Isochronal superposition”

- An isomorph-theory prediction

17356

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2005, 109, 17356–17360
Published on Web 08/30/2005

Do Theories of the Glass Transition, in which the Structural Relaxation Time Does Not Define the Dispersion of the Structural Relaxation, Need Revision?

K. L. Ngai,^{*,†} R. Casalini,^{†,‡} S. Capaccioli,^{§,||} M. Paluch,[⊥] and C. M. Roland[†]

Finding: Whether the relaxation time is increased by decreasing temperature or by increasing pressure, the effect is the same on the spectrum. Does not work for hydrogen-bonding liquids.

See also C. M. Roland, *Soft Matter* **4**, 2316 (2008).



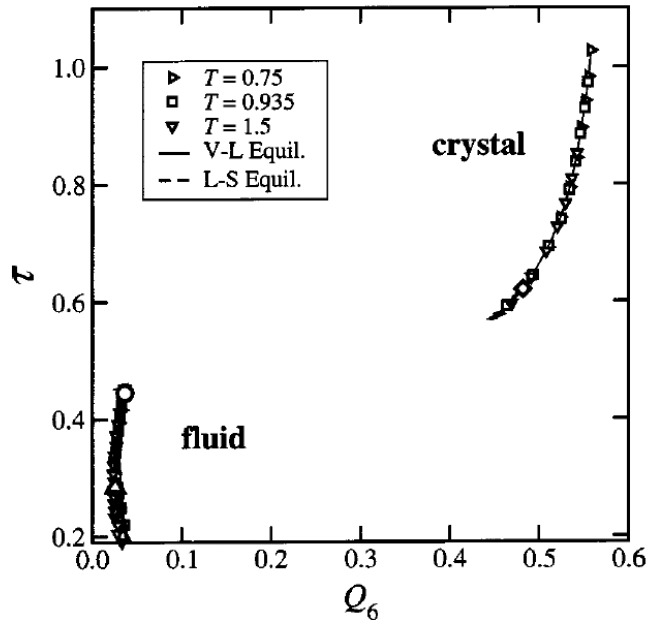
Connecting to conventional liquid state theory

- 1) The melting line is almost an isomorph. Thus the Lindemann melting criterion must be pressure independent.
- 2) Rosenfeld's "excess entropy scaling" (1977): Transport coefficients (in reduced units) are functions of the excess entropy.

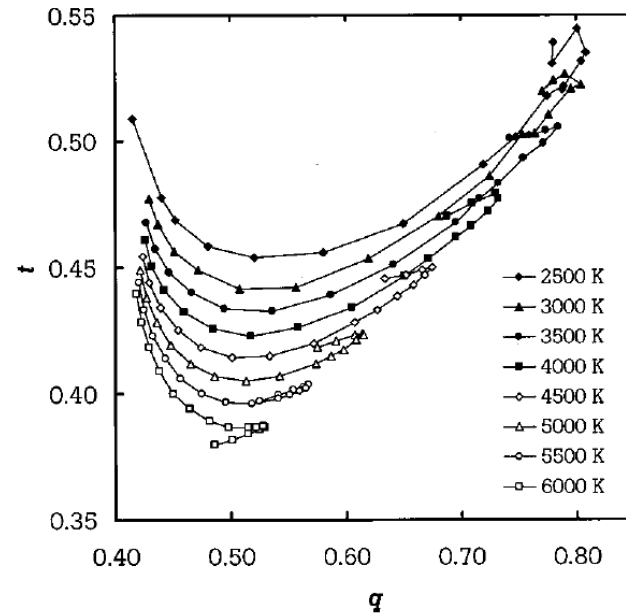


Order-parameter maps

Lennard-Jones:



BKS silica:



[Errington, Debenedetti, Torquato, J. Chem. Phys. **118**, 2256 (2003)]

[Shell, Debenedetti, Panagiotopoulos, Phys. Rev. E **66**, 011202 (2002)]



The isomorph filter

Wanted: A theory for the super-Arrhenius temperature dependence

IF a universal theory is aimed at, the quantity controlling the relaxation time must be an isomorph invariant.



Some phenomenological models

- 1) Adam-Gibbs entropy model: $\tau = \tau_0 \exp(A/TS_C)$ -
- 2) Free-volume model: $\tau = \tau_0 \exp(B/v_f)$ -
- 3) Energy controlled models: $\tau = \tau_0 \exp((E_0 - \langle E \rangle) / k_B T)$ -
- 4) Elastic models:
 - 4a) Shoving model: $\tau = \tau_0 \exp(V_c G_\infty / k_B T)$ +
 - 4b) MSD version: $\tau = \tau_0 \exp(\rho^{-2/3} / \langle u^2 \rangle)$ +
 - 4c) Leporini version: $\tau = \tau_0 F(a^2 / \langle u^2 \rangle)$ -



Experimental validation

[Nat. Phys. 7, 816 (2011), with Mike Roland *et al.*]

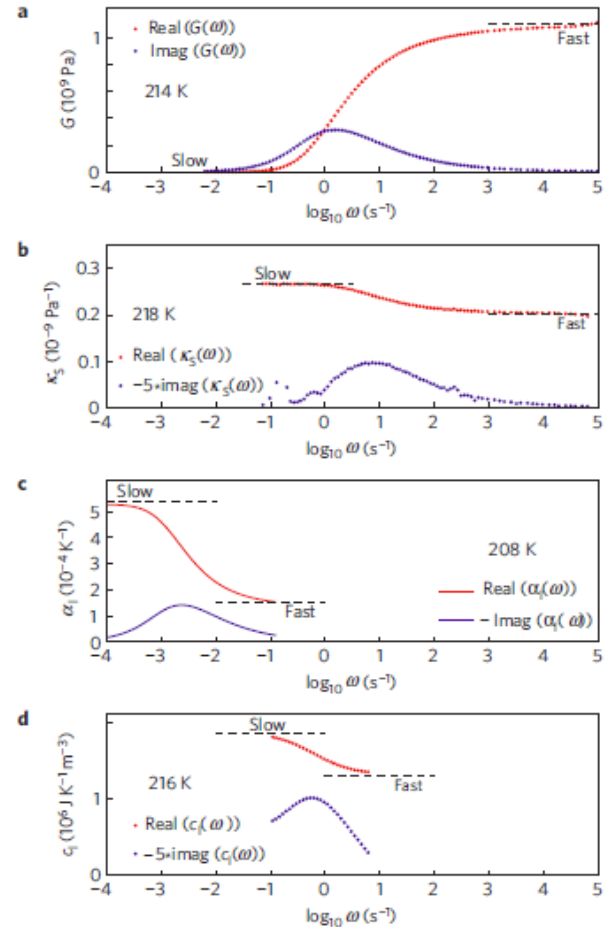
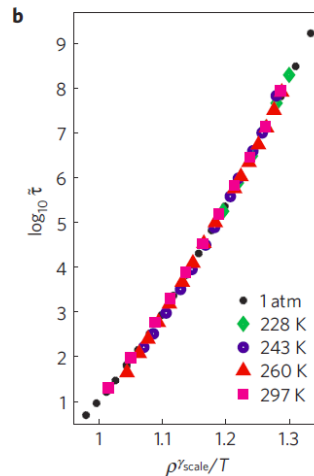
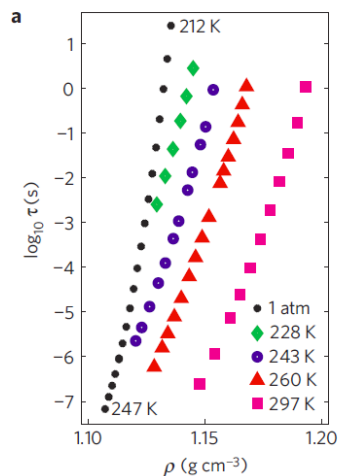
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Predicting the density-scaling exponent of a glass-forming liquid from Prigogine-Defay ratio measurements

Ditte Gundermann¹, Ulf R. Pedersen², Tina Hecksher¹, Nicholas P. Bailey¹, Bo Jakobsen¹, Tage Christensen¹, Niels B. Olsen¹, Thomas B. Schröder¹, Daniel Fragiadakis³, Riccardo Casalini³, C. Michael Roland³, Jeppe C. Dyre¹ and Kristine Niss^{1*}



Summary (part I)

van der Waals liquids and metallic liquids
(not hydrogen-bonding, ionic, covalent)
are simpler than liquids in general

These “R-simple” liquids:

- have a hidden scale invariance (part II)
- are “single-parameter liquids”
- have **isomorphs**

The *isomorph filter* allows one to sort among theories for the non-Arrhenius temperature dependence

