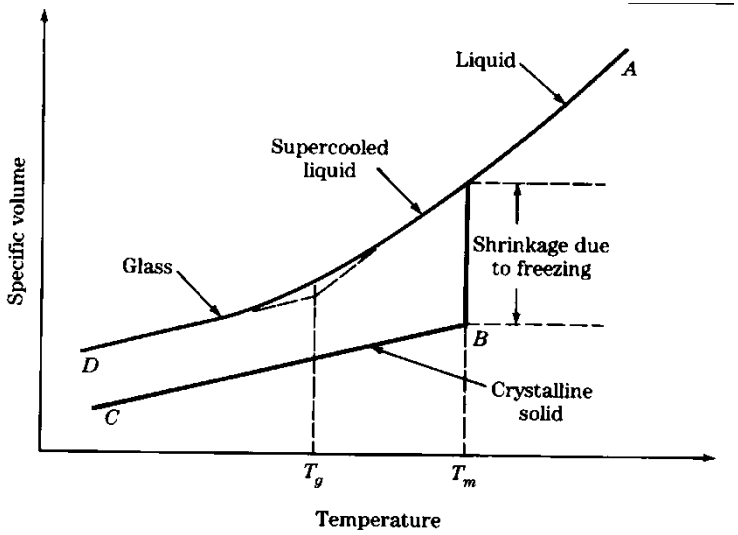
Entropy and relaxation time

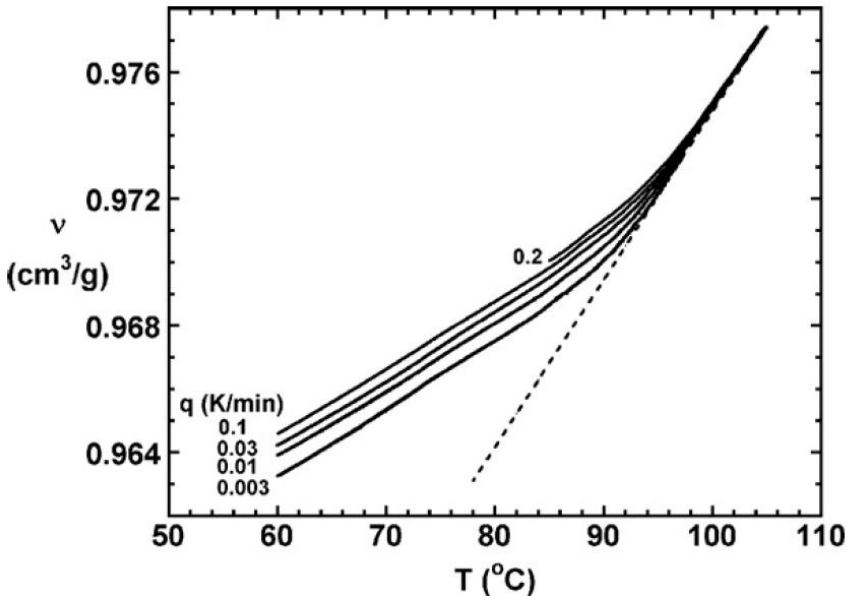
Jeppe Dyre, Roskilde University, Denmark.

Symposium on Fragility
Bengaluru, January 5, 2014.

Glass and Time – DNRF Centre for Viscous Liquid Dynamics, Roskilde University

The formation of a glass



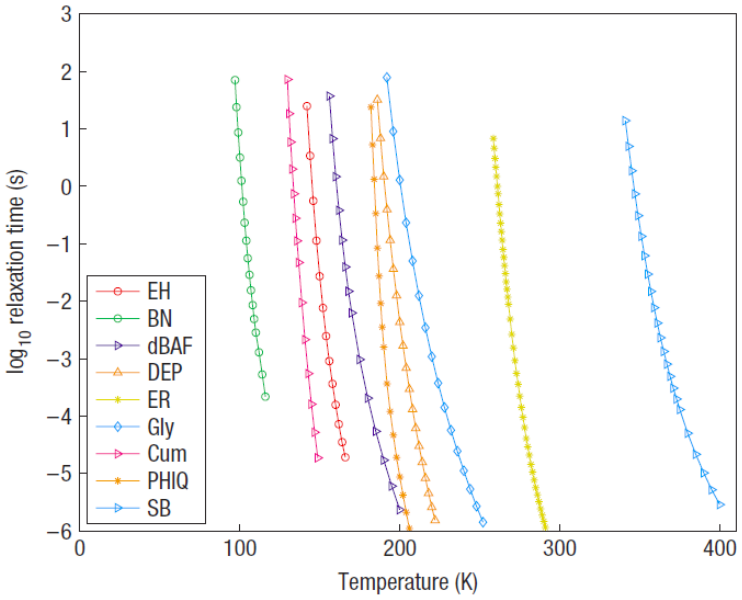


Polystyrene

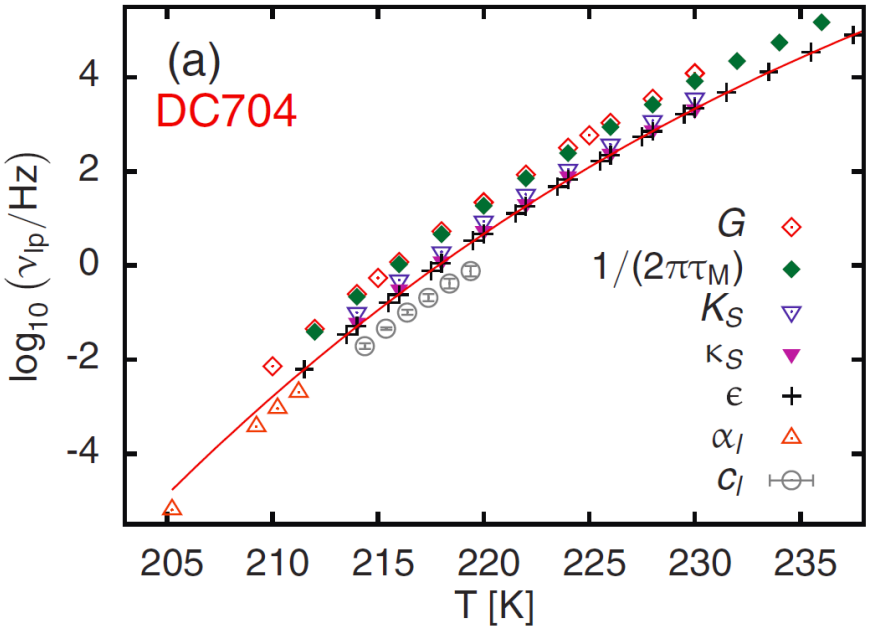
[Badrinarayanan *et al.,* J. Non-Cryst. Solids **353**, 2603 (2007)]

Glass formation: Not a phase transition

Rise of the relaxation time upon cooling

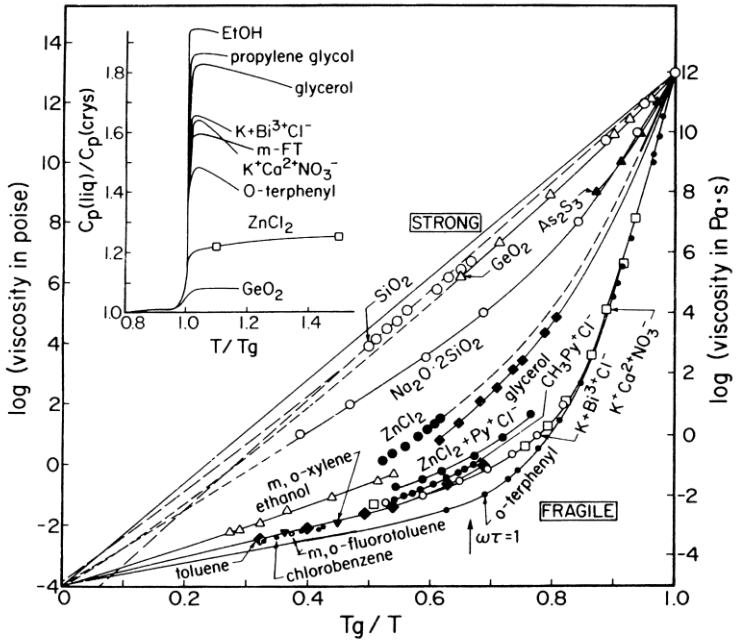


[Hecksher *et al*., Nature Phys. **4**, 737 (2008)]



[Jakobsen *et* al., JCP **136**, 081102 (2012)]

The non-Arrhenius challenge



[C. A. Angell (1985): Fragility $m = d\log(\eta)/d(T_g/T)$ evaluated at Tg.]

Entropy models

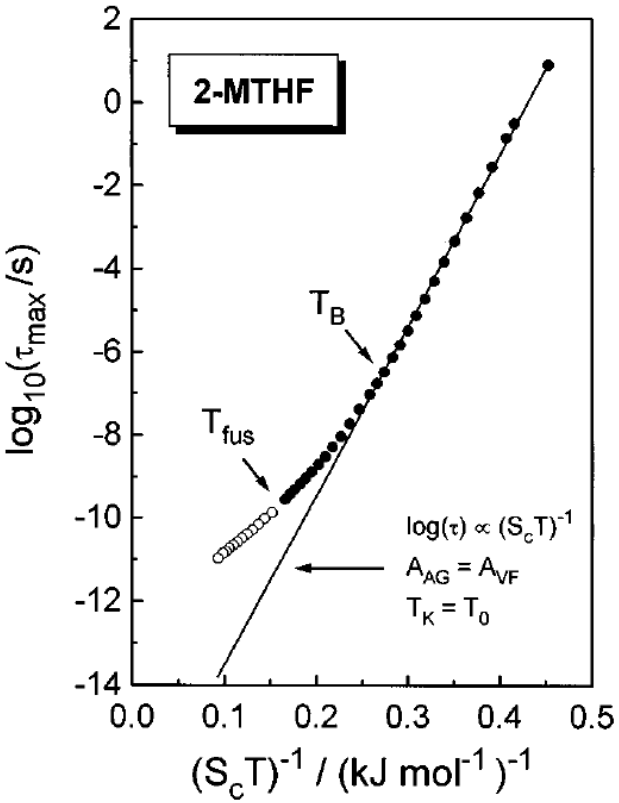
1) Bestul and Chang (1964): The glass transition takes place at a definite value of the excess entropy

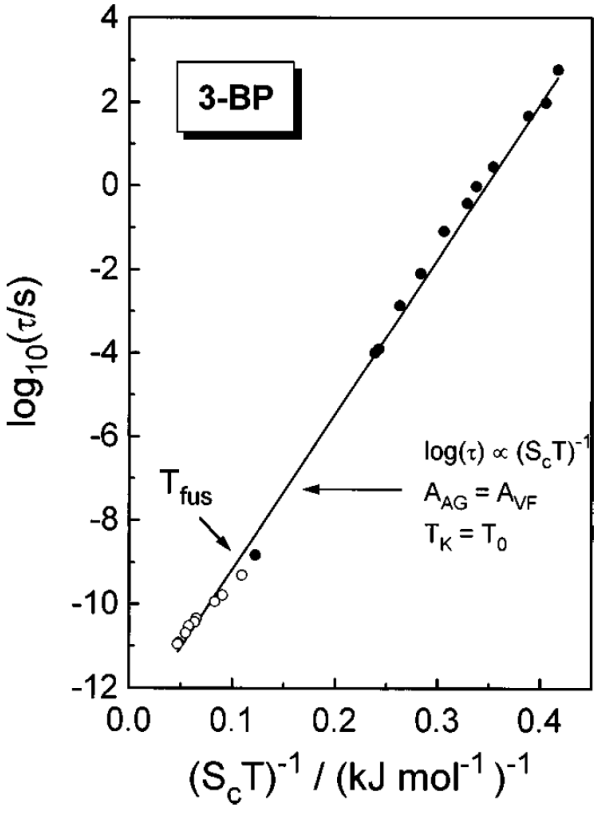
2) Adam and Gibbs (1965): $\tau = \tau_0 \exp[\frac{A}{TS_c(T)}]$

3) Rosenfeld (1977): Diffusion constant is a function of the excess entropy

4) Random First-Order Transition theory

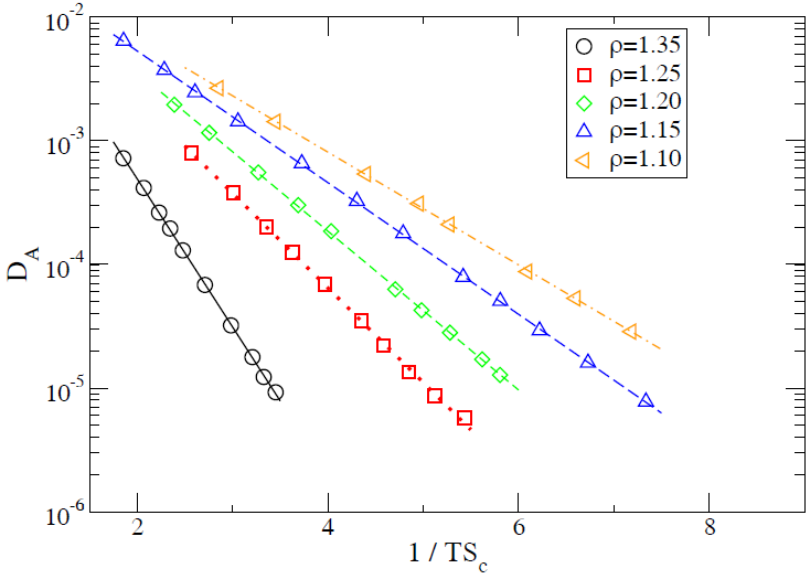
Adam-Gibbs entropy control

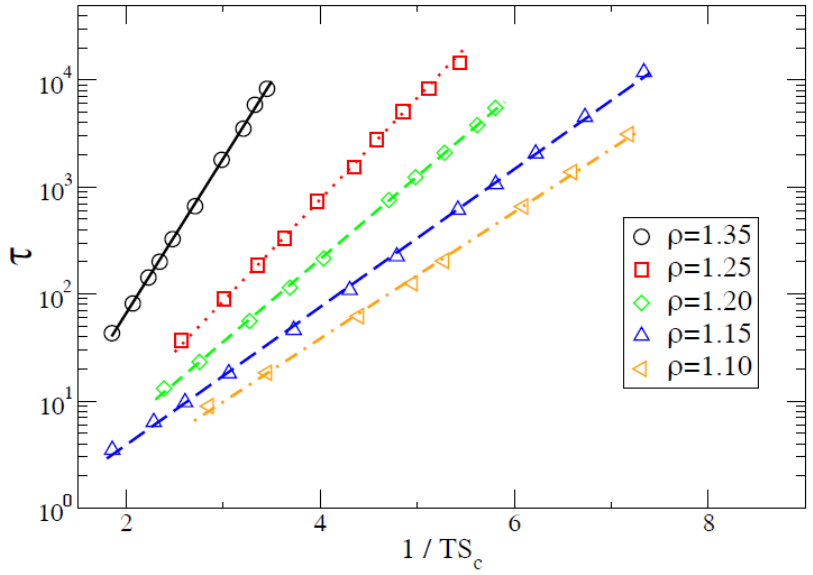




[Richert and Angell, J. Chem. Phys. **108**, 9016 (1998)]

AG evidence from simulations





[Kob-Andersen binary LJ (KABLJ) system,
Sengupta, Schrøder, Sastry, Eur. Phys J. E **36:** 141 (2013)]

Questions

1) Which entropy?
   - Bestul & Chang: Subtract ideal glass entropy
   - Adam & Gibbs: Subtract crystal entropy
   - Sastry *et al.*: Subtract vibrational entropy
   - Rosenfeld: Subtract ideal gas entropy

2) Why entropy?

Role of density

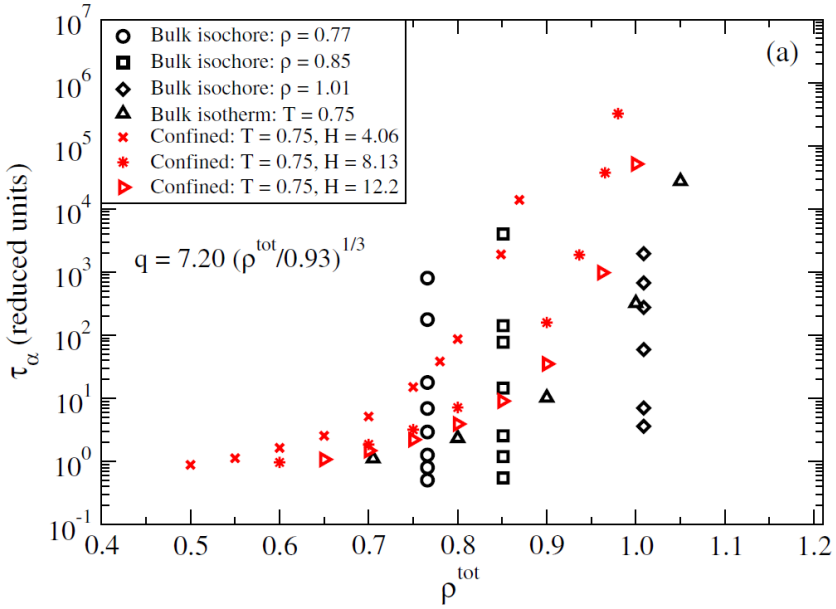
Free volume models [Doolittle (1952),
Turnbull and Cohen (1959), Cohen and Grest (1979), …]

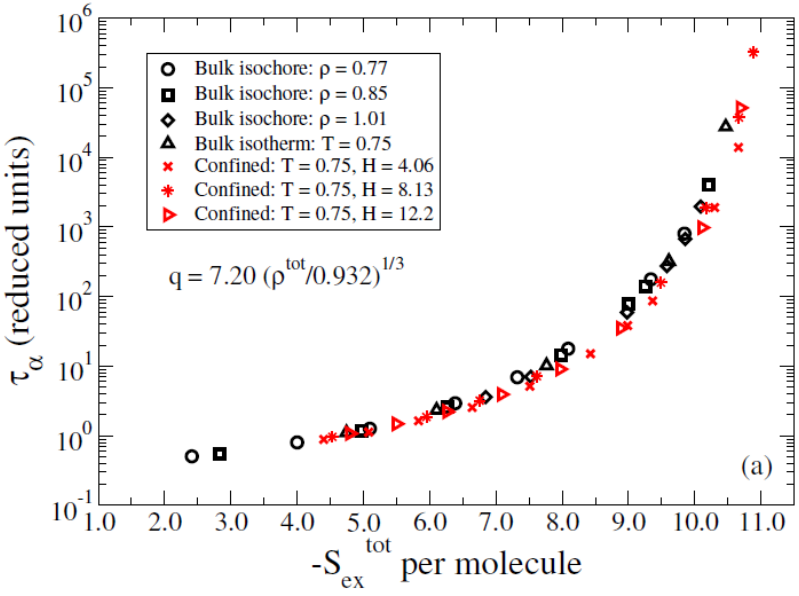
Idea:

- Relaxation time a function of density
- Modern formulation based on density control:
  Jamming scenarios

Density control?

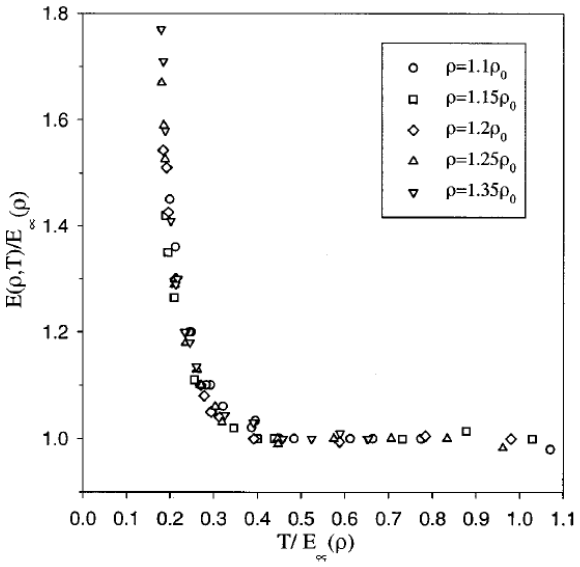
[Simulation of the asymmetric dumbbell model in bulk and confinement, Ingebrigtsen *et al*., Phys. Rev. Lett. **111**, 235901 (2013)]





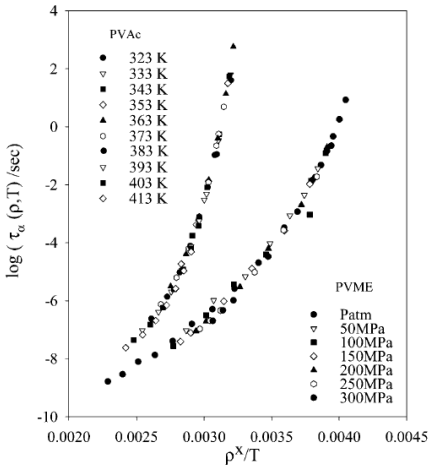
Role of density. I

[Tarjus, Kivelson, Alba-Simionesco, *et al.* (1995, 1996, 1998, 2002, 2004)]



$$\tau_\alpha(T,\rho) = \tau_\infty(\rho)\exp[E(T,\rho)/T]$$

<u>Kob-Andersen Binary Lennard-Jones (KABLJ) liquid:</u>
Activation energy and temperature have a common, density-dependent scale

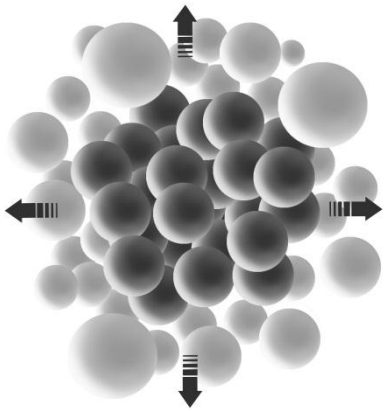


$$\log\left(\tau_\alpha(\rho,T)\right) = F\left(\frac{e(\rho)}{T}\right)$$

Role of density. II
The shoving model

[JCD, N. B. Olsen, T. Christensen, Phys. Rev. B **53**, 2171 (1996)]

$$\tau = \tau_0 \exp[V_C G_\infty(T)/k_B T]$$



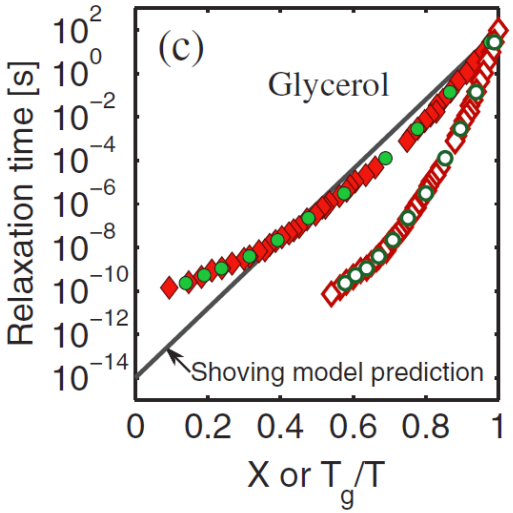
One of several ”elastic” models dating back to the 1940’s and 1950’s.

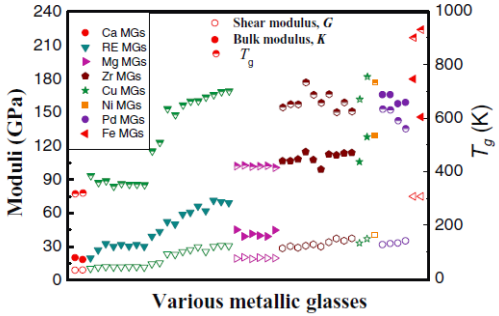
Common theme: High-frequency elastic moduli determine the activation energy.

Brief review: JCD, Rev. Mod. Phys. **78**, 953 (2006).

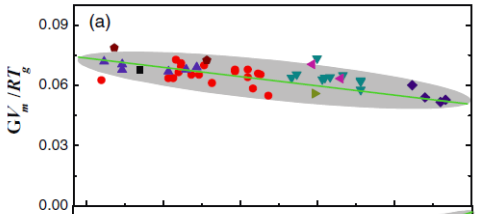
Comparison to experiment

B. Zhang *et* al., Phys. Rev. B **76**, 012201 (2007) (classical ultrasonics).
D. Torchinsky *et al*., J. Chem. Phys. **130**, 064502 (2009) (stimulated scattering).
B. Xu and G. B. McKenna, J. Chem. Phys. **134**, 124902 (2011) (rheological data).
T. Rouxel, J. Chem. Phys. **134**, 124902 (2011) (ultrasonics, Brillouin, vibrational).
W. H. Wang, J. Appl. Phys. **110**, 053521 (2011) (calorimetry; metallic glasses).
JCD and W. H. Wang, J. Chem. Phys **136**, 224108 (2012) (ditto).
C. Klieber *et al*, J. Chem. Phys. **138**, 12A544 (2013) (stim. scatt.; organic liquids).





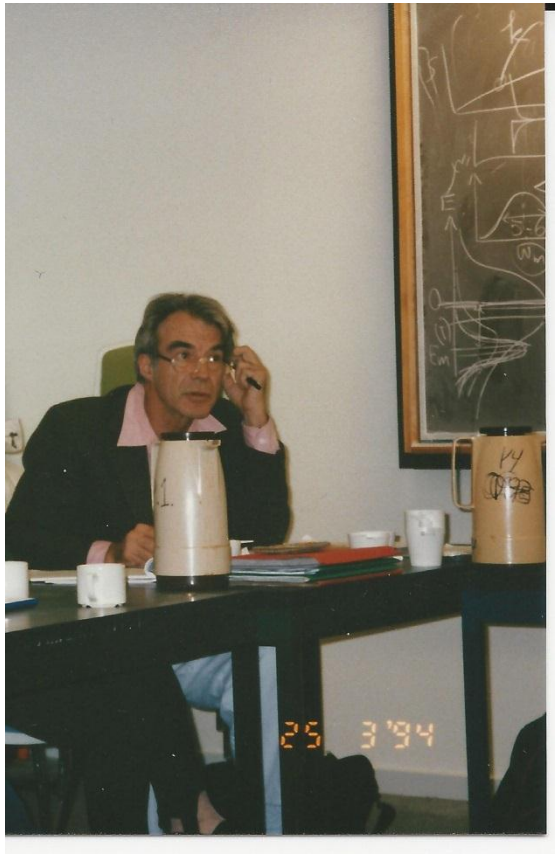
[JCP **136**, 224108 (2012)]



Poisson ratio

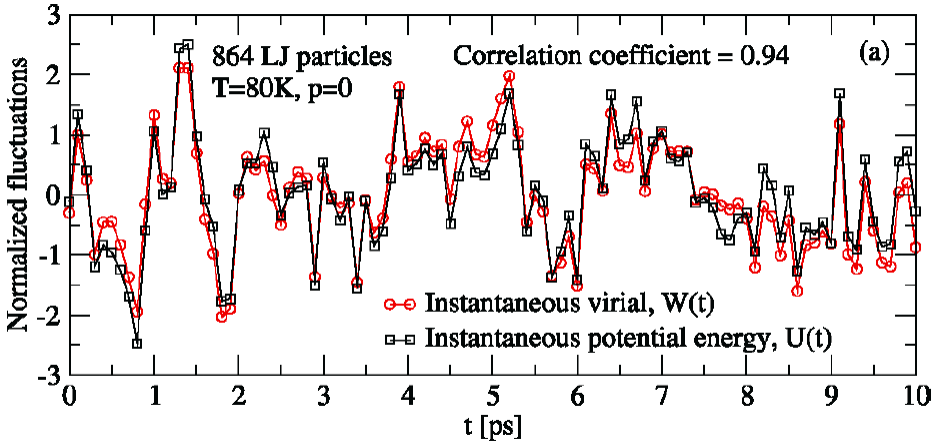
[Klieber *et* al., J. Chem. Phys. **138**, 12A544 (2013)]

"Viscous liquids and the glass transition", Roskilde, March 1994



Glass and Time – DNRF Centre for Viscous Liquid Dynamics, Roskilde University

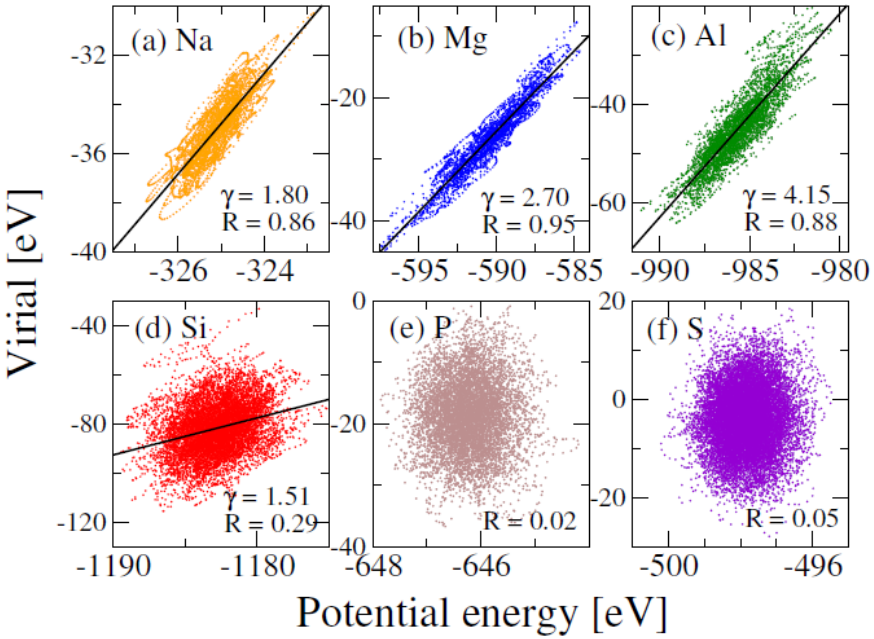
Simple liquids – Roskilde definition
(”strongly correlating”)



$$pV = Nk_BT + W$$

[Lennard-Jones system at typical liquid conditions, *NVT* simulation, Pedersen *et* al., Phys. Rev. Lett. **100**, 015701 (2008); J. Chem. Phys. **129**, 184507 and 184508 (2008).]

Ab-initio simulations
Group III elements at the triple point



[unpublised; with Hummel, Kresse, and Pedersen, Vienna]

Systems studied by simulation

Model systems with strong WU correlations (NVT ensemble):

- Inverse Power-Law systems
- LJ systems, also $v(r) = (r^{-12} + r^{-6})/2$
- Exponential potential [unpublished], Buckingham, …
- Molecular models (e.g., OTP, asymmetric dumbbell)
- Nanoconfined systems [PRL **111**, 235901 (2013)]
- Polymer models, e.g., flexible LJ chain [arXiv1307.5237]
- Crystals (LJ) [unpublished]

Exceptions: Water, methanol, …

Names:

”~~Strongly-correlating~~ liquids”
”~~Simple~~ liquids”
”Roskilde-simple liquids”
[PRX **2**, 011011 (2012); JCP **138**, 154505 (2013); PRE **88**, 042139 (2013)]

Simple liquids have isomorphic curves in the thermodynamic phase diagram

Two state points are ”isomorphic” [Gnan *et al,* JCP **131**, 234504 (2009)] if all physically relevant microconfigurations of the two state points that scale into one another - $\rho_1^{1/3}\mathbf{R}_1 = \rho_2^{1/3}\mathbf{R}_2$ - obey

$$\exp\left(-\frac{U(\mathbf{R}_1)}{k_B T_1}\right) = C_{12}\,\exp\left(-\frac{U(\mathbf{R}_2)}{k_B T_2}\right)$$

- This equation defines an equivalence relation in the thermodynamic phase diagram
- Only inverse-power-law liquids have exact isomorphs

Reduced units: Macroscopic

Length unit: $\rho^{-1/3}$

Time unit: $\rho^{-1/3}\sqrt{m/k_BT}$

Energy unit: k_BT

Isomorph properties

1) Isomorphic state points have same excess entropy. $S_{ex} = k_B \sum_i P_i \ln P_i$
2) Isomorphic state points have same excess isochoric specific heat. $C_{V,ex} = \left\langle (\Delta U)^2 \right\rangle / k_B T^2$
3) Isomorphic state points have same reduced g(r).
4) Isomorphic state points have same reduced dynamics (Newton or Brownian).
5) Isomorphic state points have same reduced relaxation time.
6) Jumps between two isomorphic state points thermalize immediately
7) ….

[JCP **131**, 234504 (2009); PRL **104**, 125902 (2010); JCP **134**, 164505 (2011);
Brief review: J. Non-Cryst. Solids **357**, 320 (2011)]

Thermodynamics of strongly correlating liquids

[Ingebrigtsen *et al.,* JCP **136**, 061102 (2012)]

$$C_V = \phi(S) \qquad T(\partial S/\partial T)_V = \phi(S)$$

V constant:

$$\mathrm{d}S/\phi(S) = \mathrm{d}T/T$$

Equation of state:

$$T = f(s)h(\rho)$$

Density scaling [Alba-Simionesco *et al.*]

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

Grüneisen equation of state:

$$W = \gamma(\rho)U + \Phi(\rho)$$

$$\gamma = \frac{\mathrm{d}\ln h}{\mathrm{d}\ln \rho}$$

Computing at *Glass and Time*

Computer clusters:

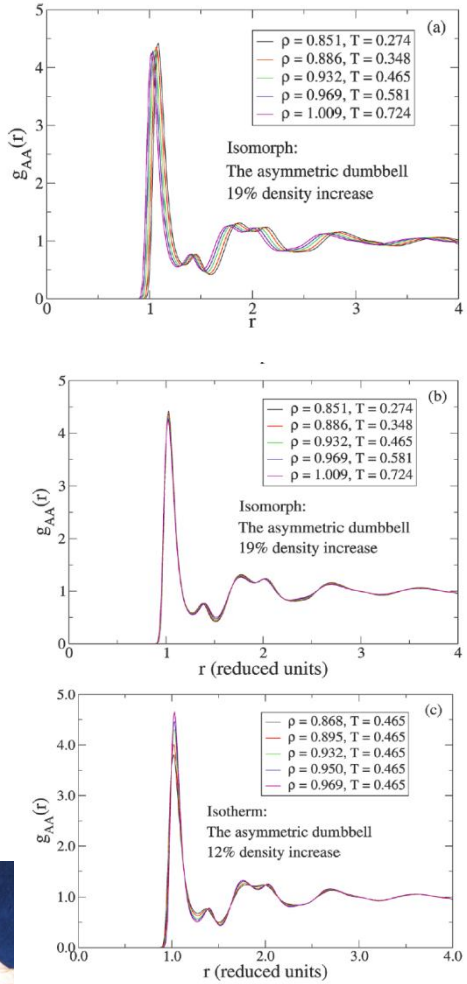
- 30 node standard cluster with dual cores (2005-…)
- An NVIDIA supercomputer with 92 GPUs, total theoretical peak performance: 85 TeraFLOPS (2008-…)
- Upgraded December 2013 to 400 TeraFLOPS

Our GPU software available at: http://rumd.org

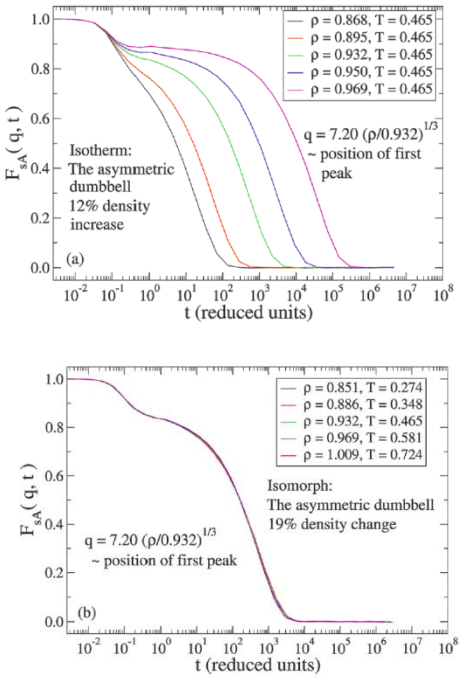
Asymmetric dumbbell model

$$\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S = \frac{\langle \Delta W \Delta U \rangle}{\langle (\Delta U)^2 \rangle}$$

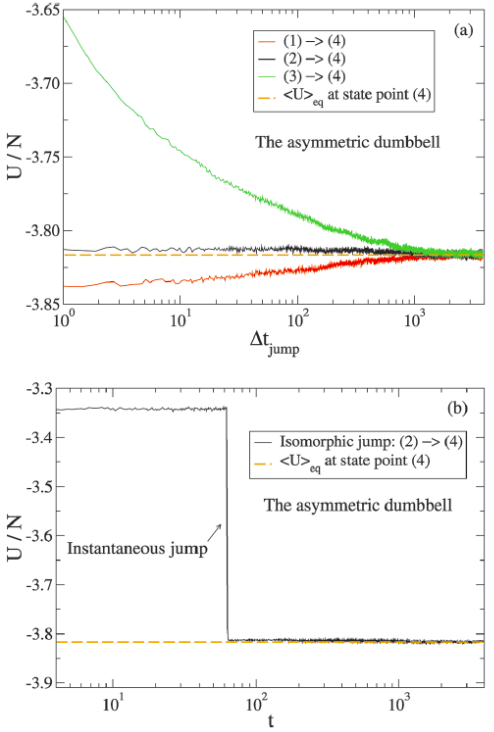
[Ingebrigtsen *et al*, JPCB **116**, 1008 (2012)]



Dynamics:

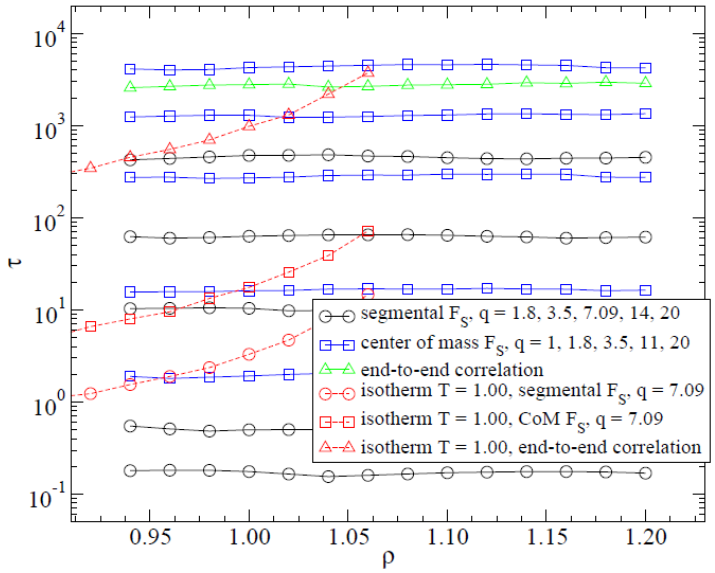


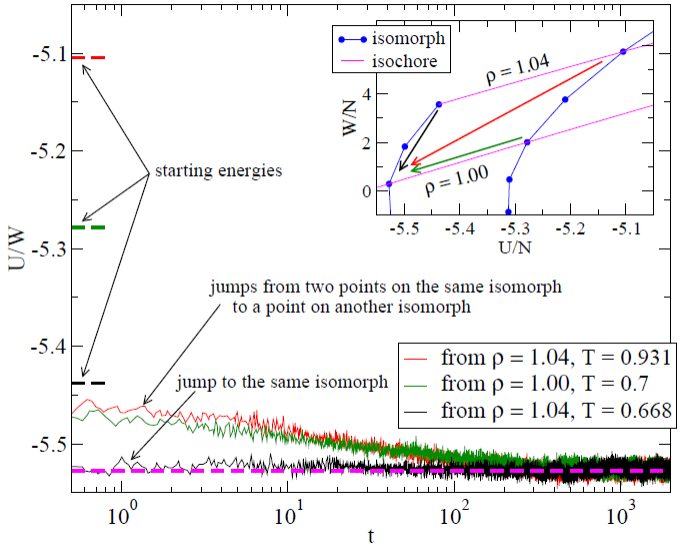
Isomorph jump:



Isomorphs for the 10-bead rigid-bond, flexible Lennard-Jones chain

[Veldhorst *et al.*, arXiv:1307.5237]

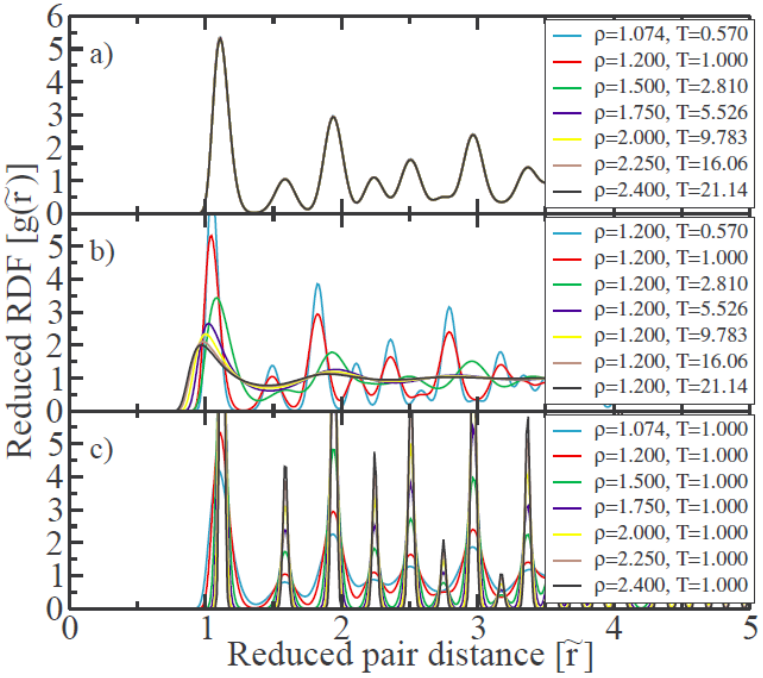


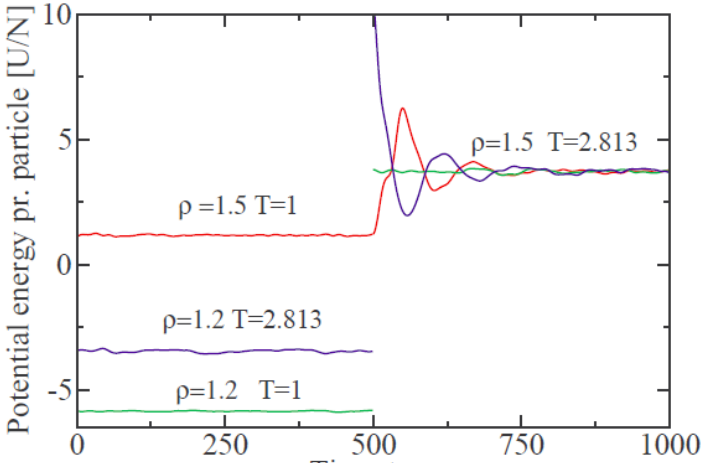


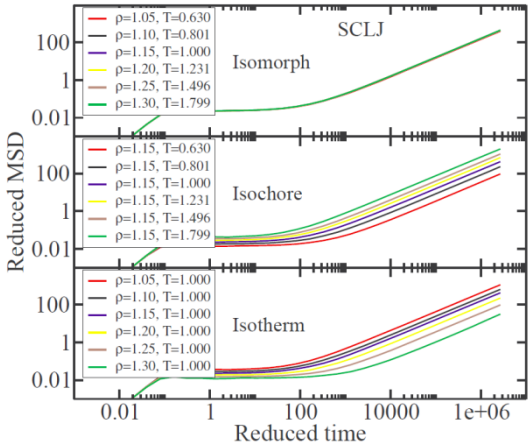
Isomorphs in crystalline systems

[Albrechtsen and Olsen, unpublished]

Lennard-Jones FCC crystal:







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”Hidden scale invariance”

[JCD, Phys. Rev. E **88**, 042139 (2013)]

”Roskilde-simple” systems obey $[\tilde{\mathbf{R}} \equiv \rho^{1/3}\mathbf{R}]$

$$U(\mathbf{R}) \cong h(\rho)\tilde{\Phi}(\tilde{\mathbf{R}}) + g(\rho)$$

Includes:
- metals
- van der Waals bonded systems
- weakly ionic/dipolar systems

Excludes:
- covalently and hydrogen-bonded systems,
- strongly charged systems

Consequences of hidden scale invariance

$$U(\mathbf{R}) \cong h(\rho)\tilde{\Phi}(\tilde{\mathbf{R}}) + g(\rho) \qquad \tilde{\mathbf{R}} \equiv \rho^{1/3}\mathbf{R}$$

$$W(\mathbf{R}) \equiv (-1/3)\mathbf{R}\cdot\nabla U(\mathbf{R}) \qquad W(\mathbf{R}) = \left(\frac{\partial U(\mathbf{R})}{\partial \ln \rho}\right)_{\tilde{\mathbf{R}}}$$

$$W(\mathbf{R}) \cong (dh/d\ln\rho)\tilde{\Phi}(\tilde{\mathbf{R}}) + dg/d\ln\rho$$

$$W(\mathbf{R}) \cong \gamma(\rho)U(\mathbf{R}) + \phi(\rho) \quad \gamma(\rho) \equiv d\ln h/d\ln\rho \qquad \Delta W(\mathbf{R}) \cong \gamma\,\Delta U(\mathbf{R})$$

Isomorphs: Given two densities and K>0. Define:

$$k_B T_1 = K\,h(\rho_1) \quad k_B T_2 = K\,h(\rho_2) \qquad U(\mathbf{R}_1) \cong h(\rho_1)\frac{U(\mathbf{R}_2)}{h(\rho_2)} + G(\rho_1,\rho_2)$$

$$\exp\left(-\frac{U(\mathbf{R}_1)}{k_B T_1}\right) = C_{12}\exp\left(-\frac{U(\mathbf{R}_2)}{k_B T_2}\right) \qquad k_B T = f(s)h(\rho)$$

Isomorph equation:

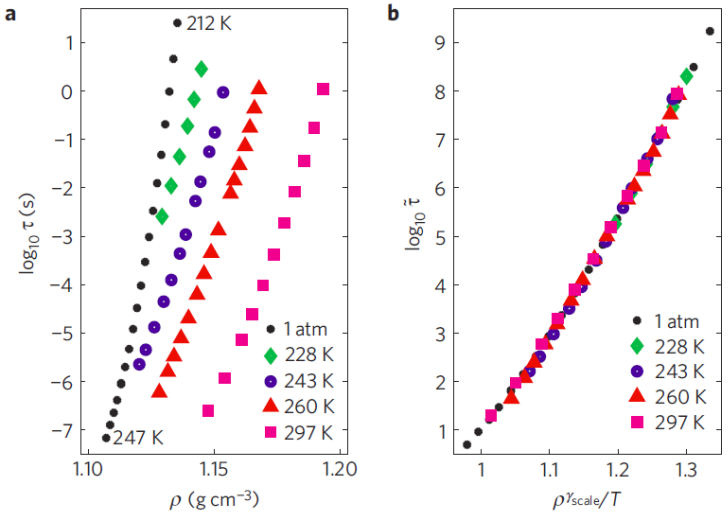
$$\frac{h(\rho)}{k_B T} = \text{Const.}$$

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

Glass and Time – DNRF Centre for Viscous Liquid Dynamics, Roskilde University

Application to glass-forming liquids. I Density scaling

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



Silicone oil DC 704
[Gundermann *et al.*, Nature Phys. **7**, 816 (2011)]
- Review: Roland *et al.*, Rep. Prog. Phys. **68**, 1405 (2005)

Exception: Hydrogen-bonded liquids

Application to glass-forming liquids. II Isochronal superposition

Same relaxation time implies same relaxation spectrum
[Tölle *et al.* (1998, 2001); Roland *et al.* (2003)]

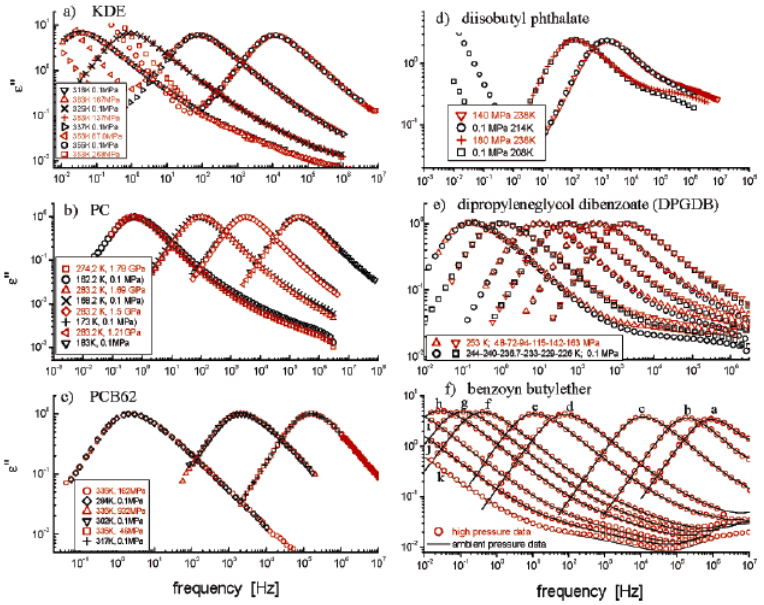
17356

THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS

2005, *109*, 17356−17360
Published on Web 08/30/2005

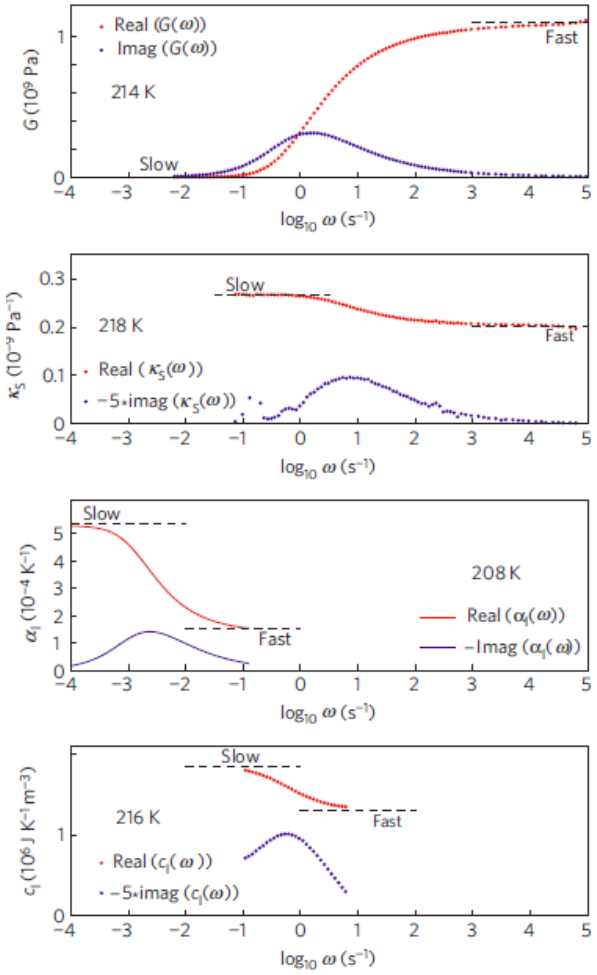
Do Theories of the Glass Transition, in which the Structural Relaxation Time Does Not Define the Dispersion of the Structural Relaxation, Need Revision?

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



Exception: Hydrogen-bonded liquids

Application to glass-forming liquids. III



ARTICLES
PUBLISHED ONLINE: 3 JULY 2011 | DOI: 10.1038/NPHYS2031
nature physics

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

Ditte Gundermann[1], Ulf R. Pedersen[2], Tina Hecksher[1], Nicholas P. Bailey[1], Bo Jakobsen[1], Tage Christensen[1], Niels B. Olsen[1], Thomas B. Schrøder[1], Daniel Fragiadakis[3], Riccardo Casalini[3], C. Michael Roland[3], Jeppe C. Dyre[1] and Kristine Niss[1]*

GLASS PHYSICS

Prigogine and Defay say relax

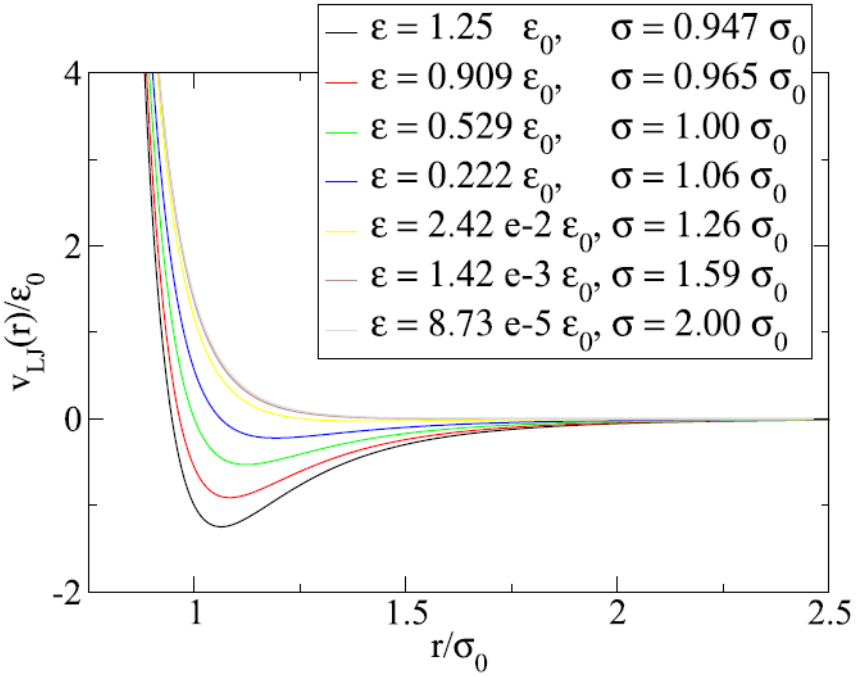
For an important class of liquids, relaxation dynamics are constrained by a surprisingly simple scaling relationship between density and temperature. It seems that thermodynamics holds the key to pinning down the exponent.

C. Austen Angell and Iolanda Santana Klein

Glass and Time – DNRF Centre for Viscous Liquid Dynamics, Roskilde University

Application to glass-forming liquids. IV
Is the liquid-state paradigm misleading?

[Berthier and Tarjus, PRL **103**, 170601 (2009)]



IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **25** (2013) 032101 (5pp) doi:10.1088/0953-8984/25/3/032101

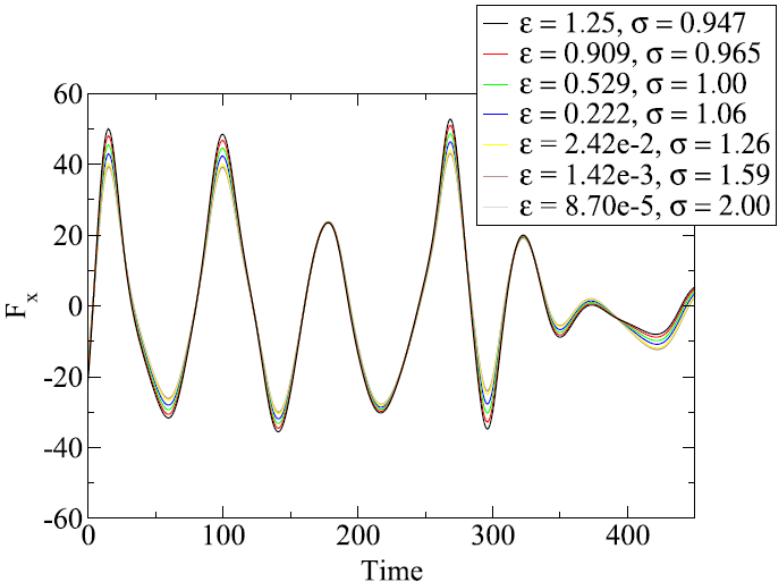
FAST TRACK COMMUNICATION

Do the repulsive and attractive pair forces play separate roles for the physics of liquids?

Lasse Bøhling, Arno A Veldhorst, Trond S Ingebrigtsen, Nicholas P Bailey, Jesper S Hansen, Søren Toxvaerd, Thomas B Schrøder and Jeppe C Dyre

[Bøhling *et* al., J. Phys. Condens. Matter **25**, 032101 (2013)]

Equivalent potentials:
Give (almost) same g(r) and dynamics.



Application to glass-forming liquids. V. ”The isomorph filter”

Wanted: A theory for the super-Arrhenius temperature dependence of glass-forming liquids’ relaxation time

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

Using the isomorph filter

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 $\tau = \tau_0 \exp((E_0 - < E >)/k_B T)$ -

4) Elastic models

4a) Shoving model: $\tau = \tau_0 \exp(V_c G_\infty / k_B T)$ +

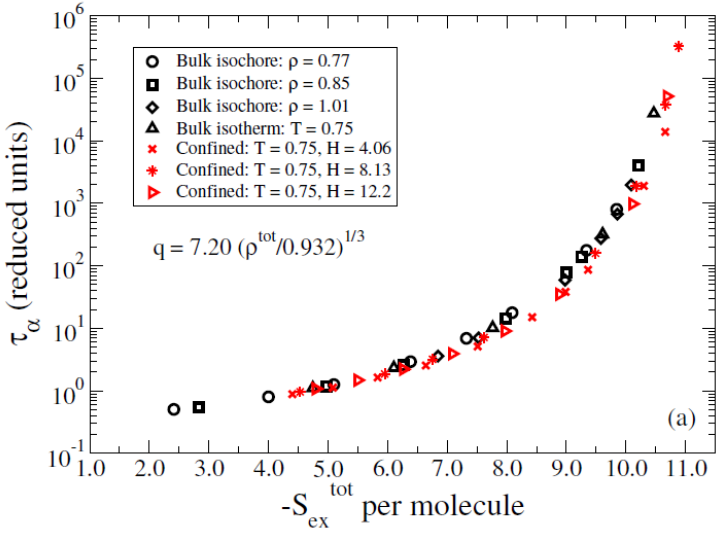
4b) MSD version: $\tau = \tau_0 \exp(\rho^{-2/3} / < u^2 >)$ +

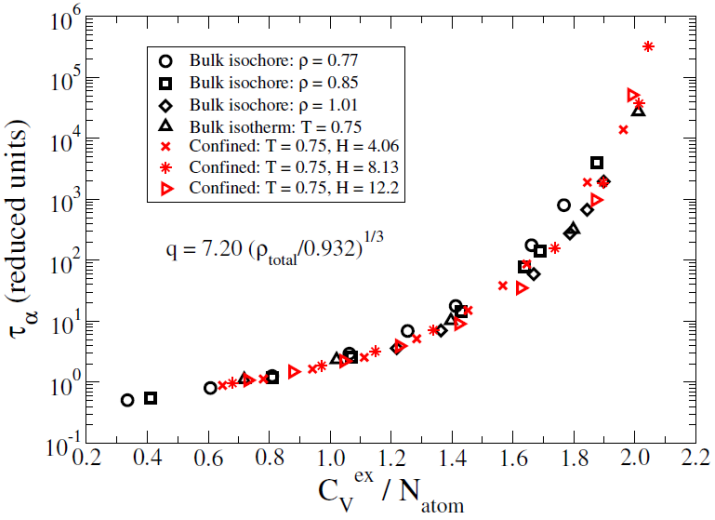
4c) Leporini version: $\tau = \tau_0 F(a^2 / < u^2 >)$ -

5) RFOT (with entropy-determined surface tension) +

Isomorph perspective on the role of entropy for the relaxation time

- Entropy is an isomorph invariant - does it controls the relaxation time?
- Any isomorph invariant ”controls” the relaxation time, example:





[Ingebrigtsen *et al*.,Phys. Rev. Lett. **111**, 235901 (2013)]

Concluding remarks

1) For Roskilde-simple liquids - van der Waals bonded, metals, weakly ionic/dipolar - several quantities ”control” the relaxation time.
2) There is no necessary causal relation.
3) The isomorph filter that can be used to rule out certain theories as not universal.
4) Does a universal theory exist of what controls the relaxation time? If yes: The primary testing ground should be non-Roskilde simple systems.