Strong Virial / Potential Energy Correlations, and the Many Consequences for Viscous Liquids

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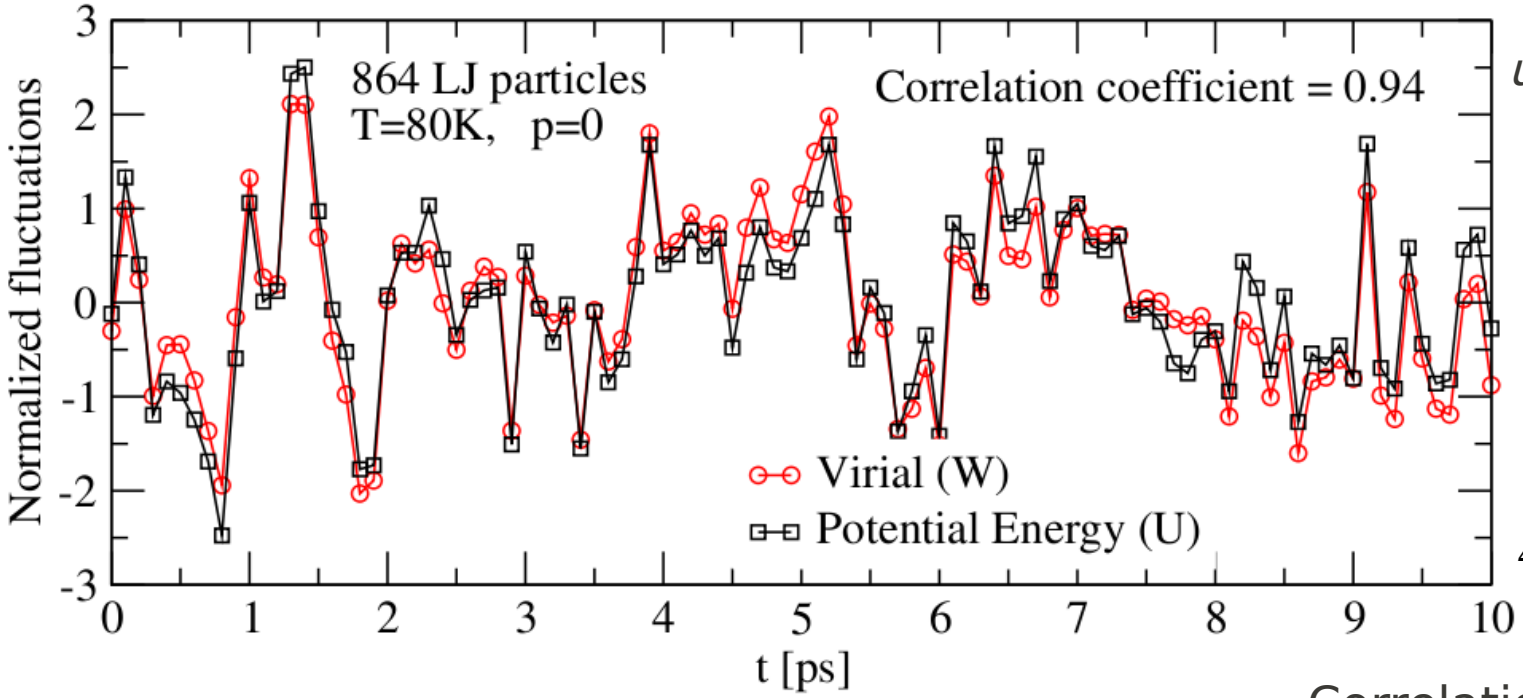
Glass and Time

Danish National Research Foundation Centre for Viscous Liquid Dynamics

The single component Lennard-Jones liquid revisited

Pressure and energy split in kinetic and configurational parts:

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



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

MD simulations
NVT-ensemble

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

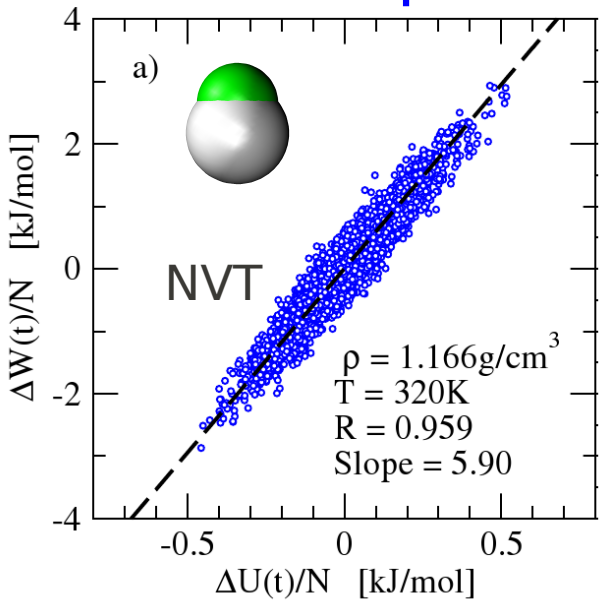
$$\Delta W(t) \equiv W(t) - \langle W \rangle$$

Correlation coefficient:

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

[Pedersen et al. PRL 100 015701 2008]

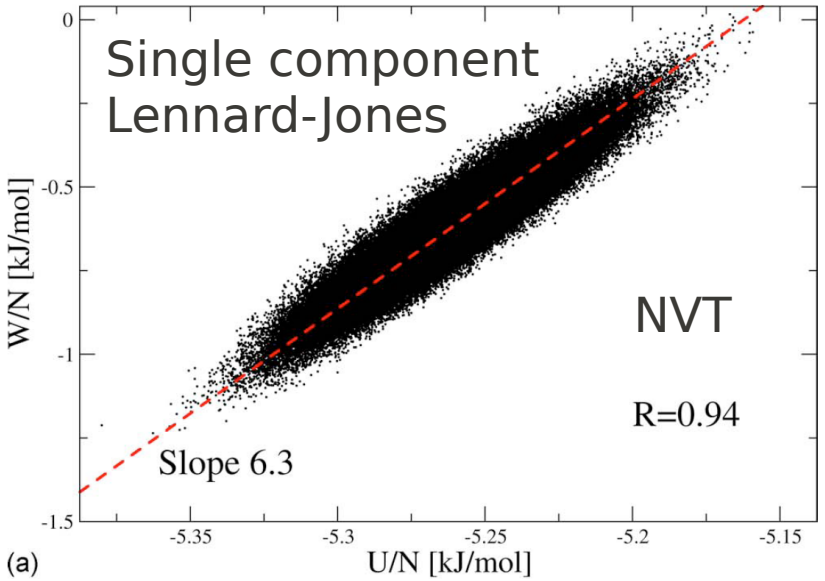
Some liquids are "strongly correlating" (R>0.9)

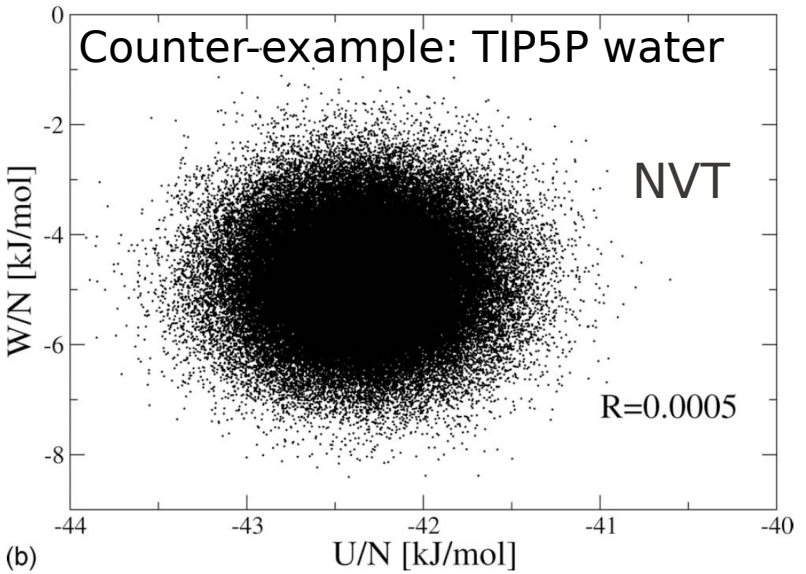


IPL (Inverse Power Law, Soft Sphere):

$$U = \sum_{pairs} u(r) = \sum_{pairs} A r^{-n}$$

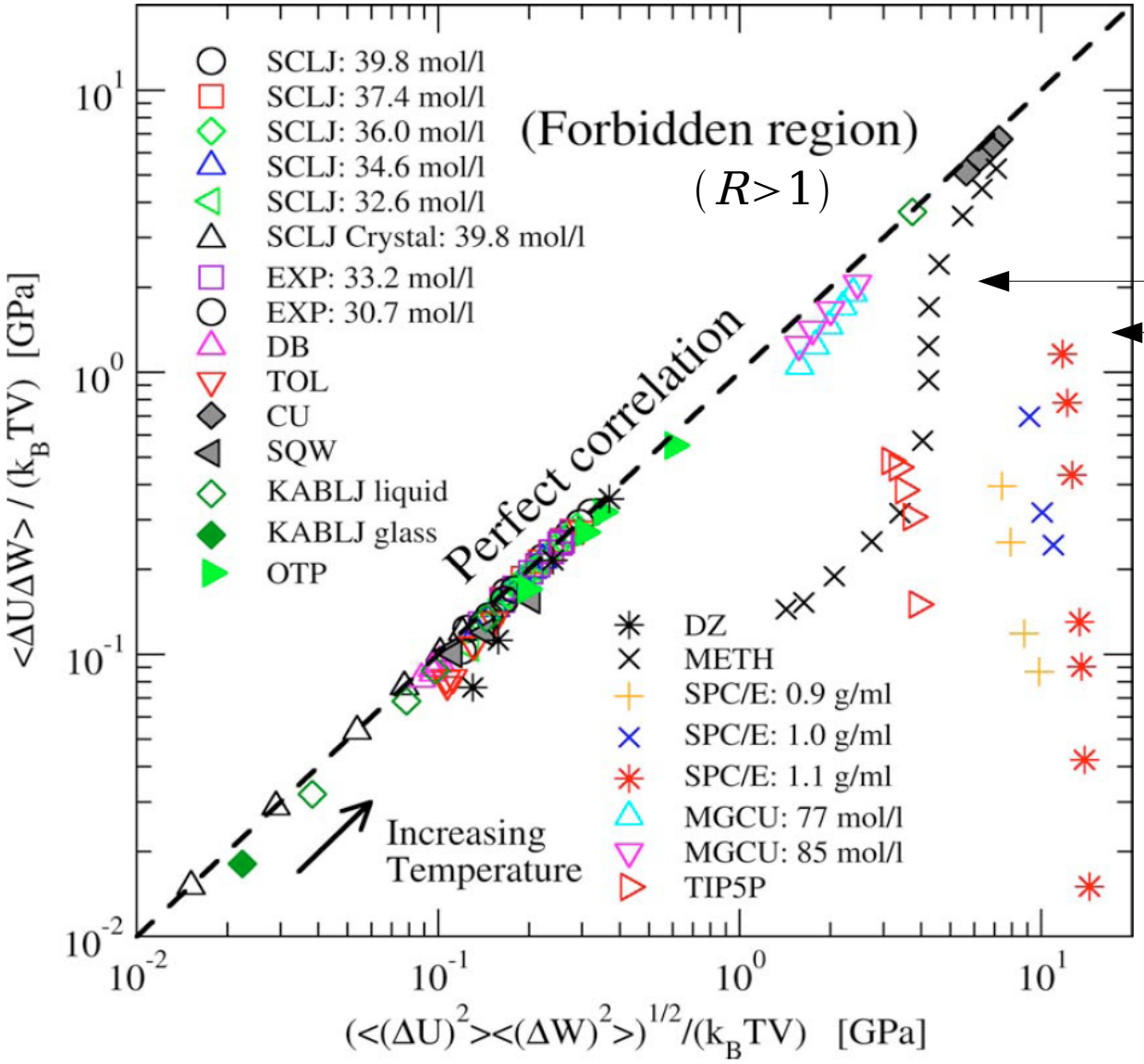
$$W \equiv -\frac{1}{3} \sum_{pairs} r \frac{\partial u(r)}{\partial r} = \frac{n}{3} U, \quad R=1$$





[Pedersen et al., PRL 100, 015701 (2008);
Bailey et al., JCP 129, 184507 (2008), paper I]

How general are the correlations?



Correlation coefficient:

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

Competing interactions destroy the correlation:

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

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

Not correlated

Correlated

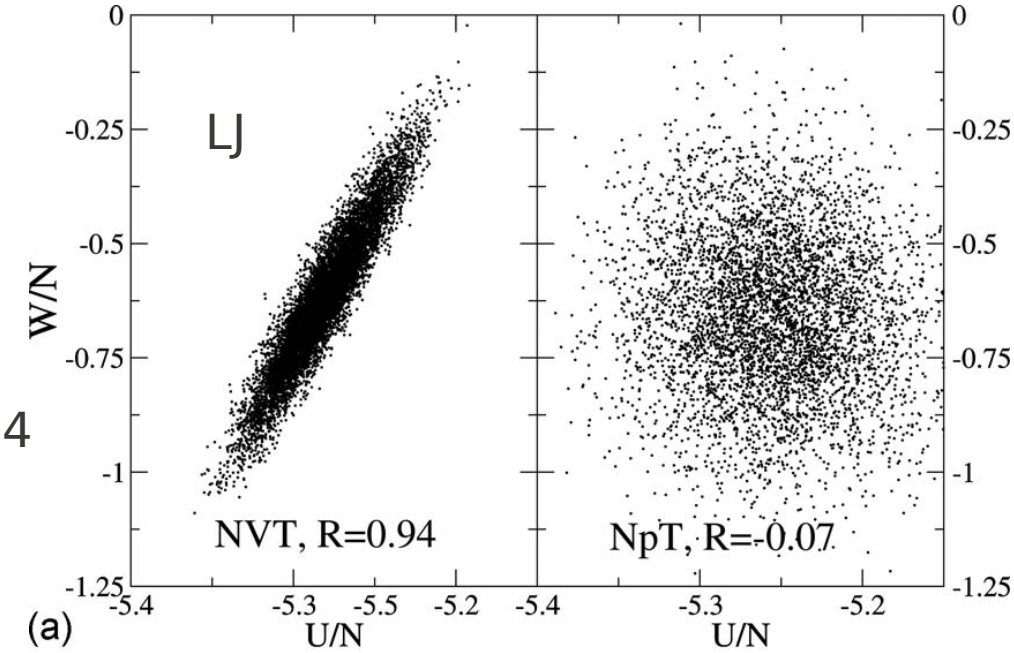
Correlated

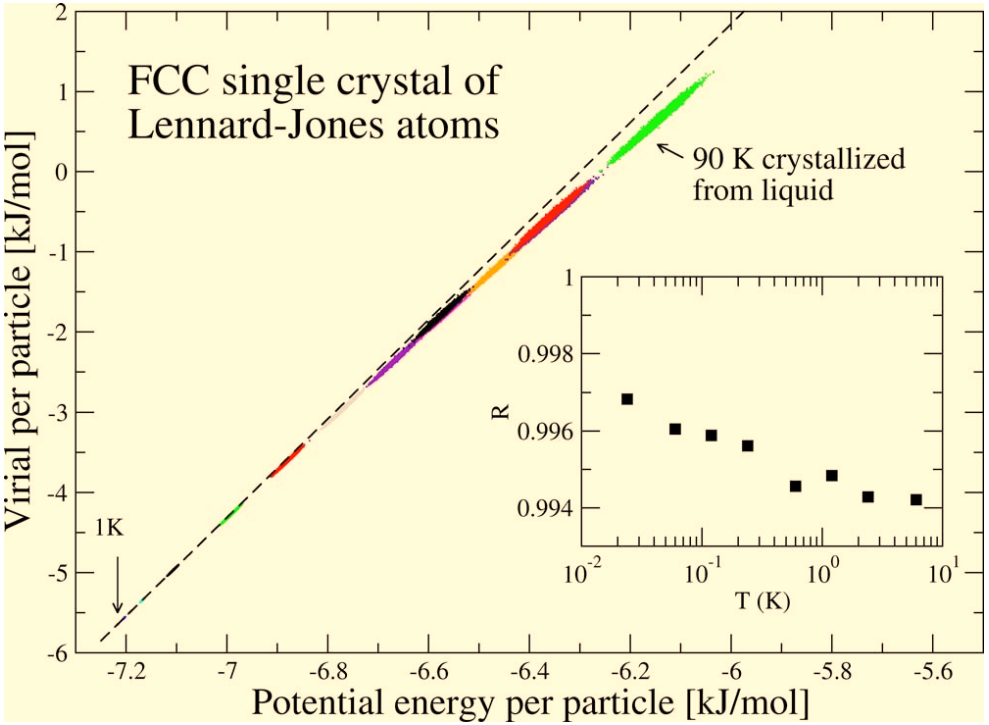
[Pedersen et al. PRL (2008)]
[Bailey et al. JCP (2008), paper I]

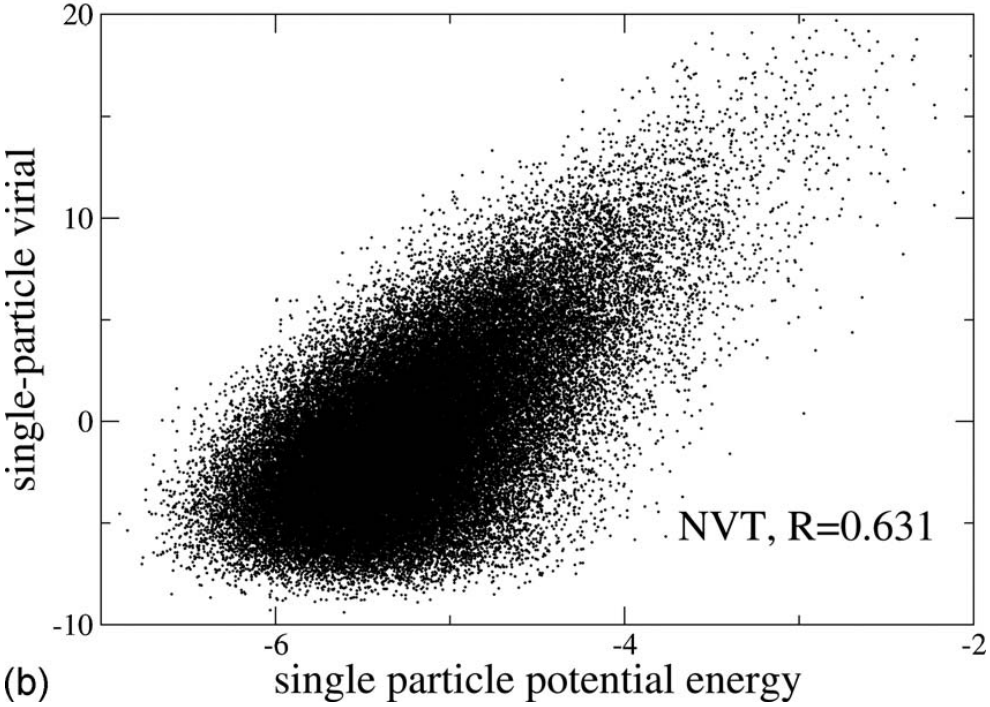
There exists a class of "strongly correlating liquids":
- including: van der Waals and (some) metals.
- excluding: hydrogen-bonding and ionic liquids.

Some findings we have to explain

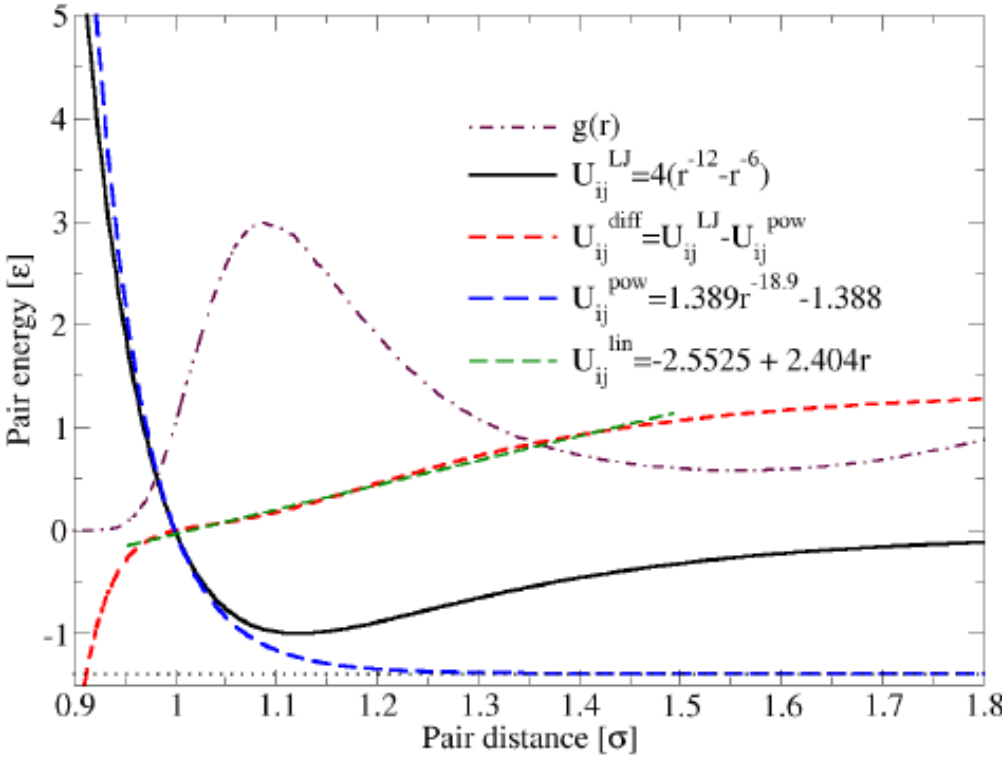
Slopes > 4







Why are there strong correlations?



$U^{LJ} - U^{pow} \simeq br + c$, in the first peak of $g(r)$:

$$U^{LJ} = ar^{-n} + br + c + U^{rest}$$

Perfect U-W correlation:

$$W \equiv -\frac{1}{3}\sum_{pairs} r\frac{\partial U(r)}{\partial r}$$

[Bailey et al., JCP 129, 184508 (2008), paper II;
Schrøder et al., JCP 131, 234503(2009), paper III]

(See also Ben-Amotz & Stell, JCP (2005))

One-dimensional system with only nearest neighbor interactions in a constant "volume" L:

$$\sum_{i>j} r_{ij} = L$$

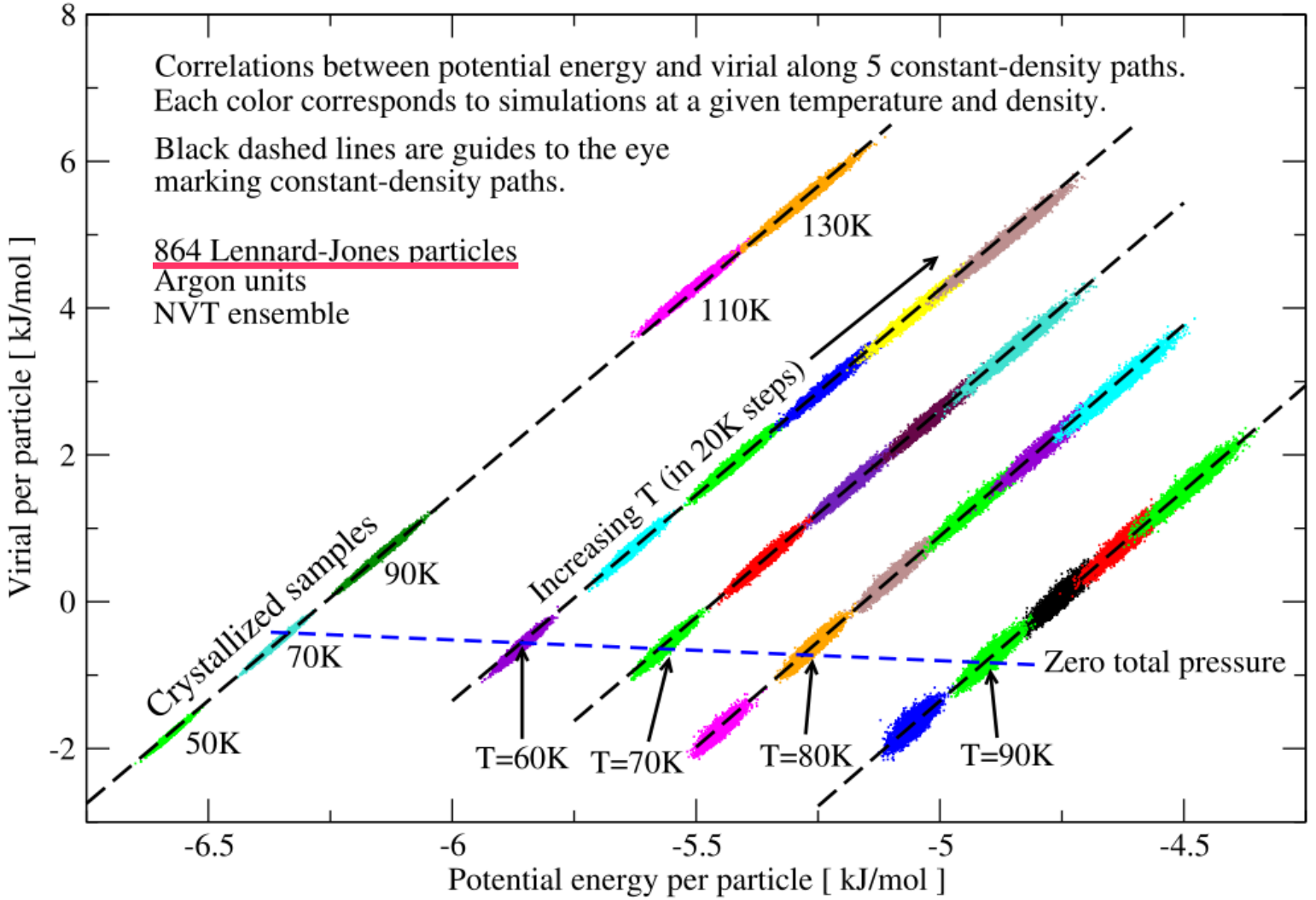
$$\Downarrow$$

$$\sum_{i>j}(br_{ij} + c) = bL + Nc = [\text{constant}]$$

3D: contribution from linear term to a good approximation only depends on density

Consequence:
Strongly correlating liquids inherit (some) scaling properties from the IPL potential:
They have a "hidden scale invariance".

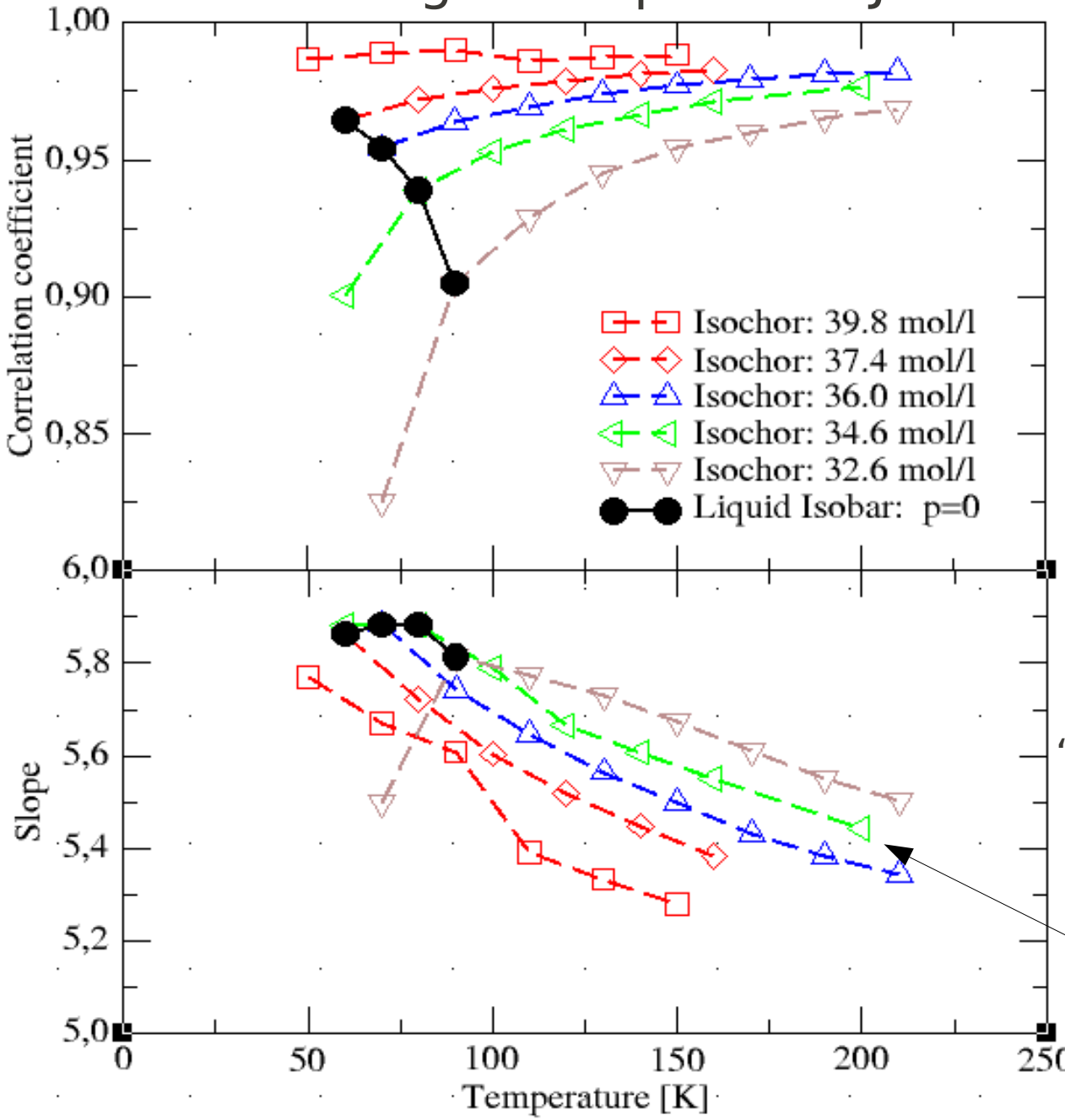
Isochores are straight lines in the W,U state diagram.



Inverse Power Law: $W = \gamma U$

[Pedersen et al., PRL 100, 015701 (2008)]

Single component LJ



Along an isochor:
Correlations increase
- with increasing T

Along an isotherm:
Correlations increase
- with increasing density

Along an isobar (p=0):
Correlations increase
- with decreasing T

"Density wins over temperature"
- important for viscous liquids!

Slopes (n/3) very slowly goes to 4 (as they should)
[r^(-12) eventually dominates]
T=1000K : Slope = 4.6

Experimental consequences, Argon

If we can subtract of kinetic terms:

$$\frac{\langle (\Delta U)^2 \rangle}{k_B T^2} = C_V - \frac{3}{2} N k_B = C_V^{conf}$$

$$\frac{\langle \Delta U \Delta W \rangle}{k_B T^2} = V\beta_V - N k_B = V\beta_V^{conf}$$

$$\frac{\langle (\Delta W)^2 \rangle}{k_B T V} = \frac{N k_B T}{V} + \frac{W}{V} - K_T + \frac{X}{V}$$

The hypervirial:

$X = \sum_{pairs} X(r)/9$, where $X(r) = rW'(r)$

Correlation coefficient squared:

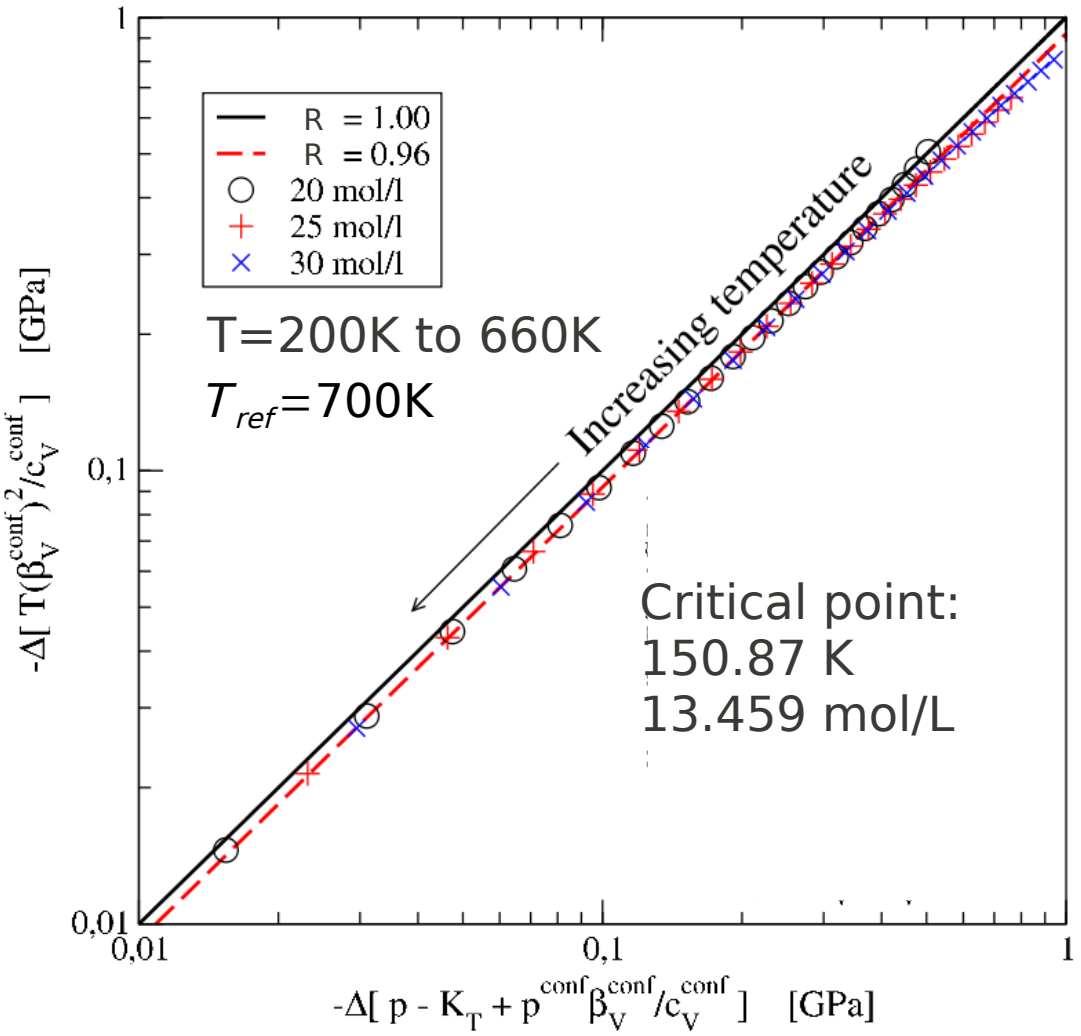
$$R^2 \equiv \frac{\langle \Delta W \Delta U \rangle^2}{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle} \Rightarrow$$

$$T\frac{\left(\beta_V^{conf}\right)^2}{C_V^{conf}/V} = R^2\left(p - K_T + \frac{X}{V}\right) =$$

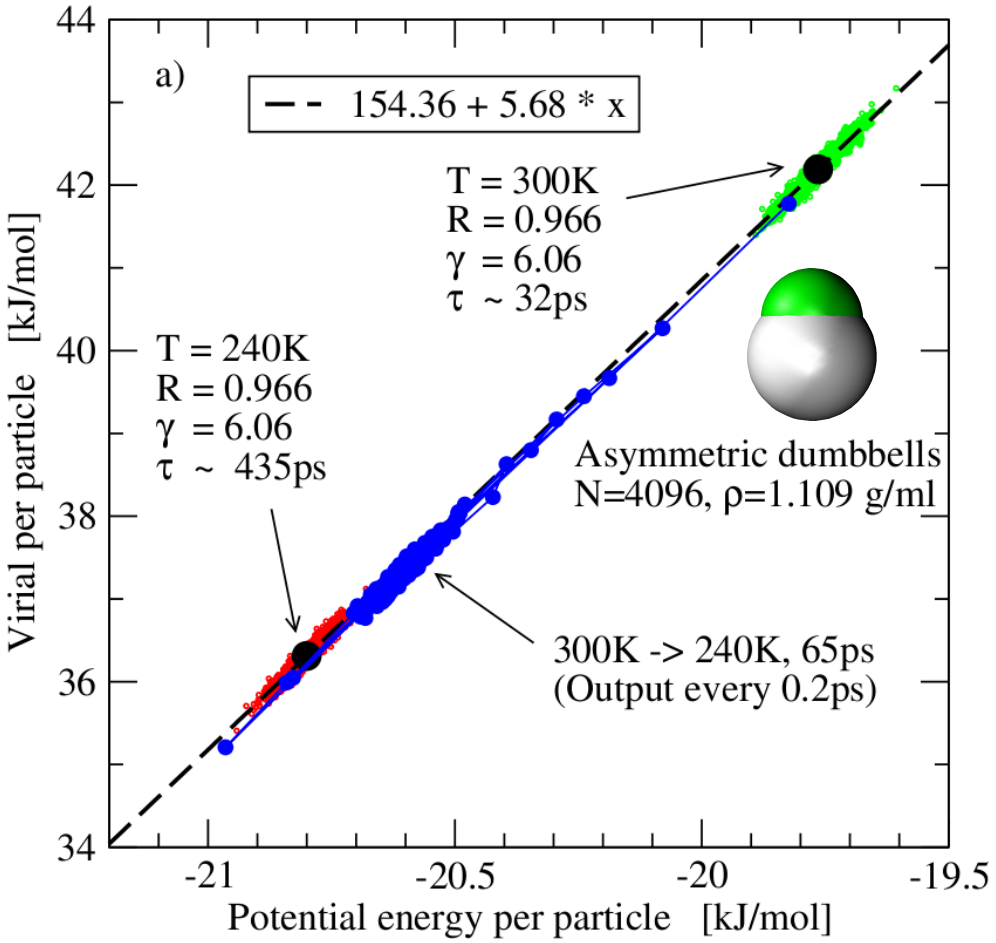
Approximations:

1: $X - X_{ref} = \frac{n}{3}\left(W - W_{ref}\right)$, 2: R (roughly) constant

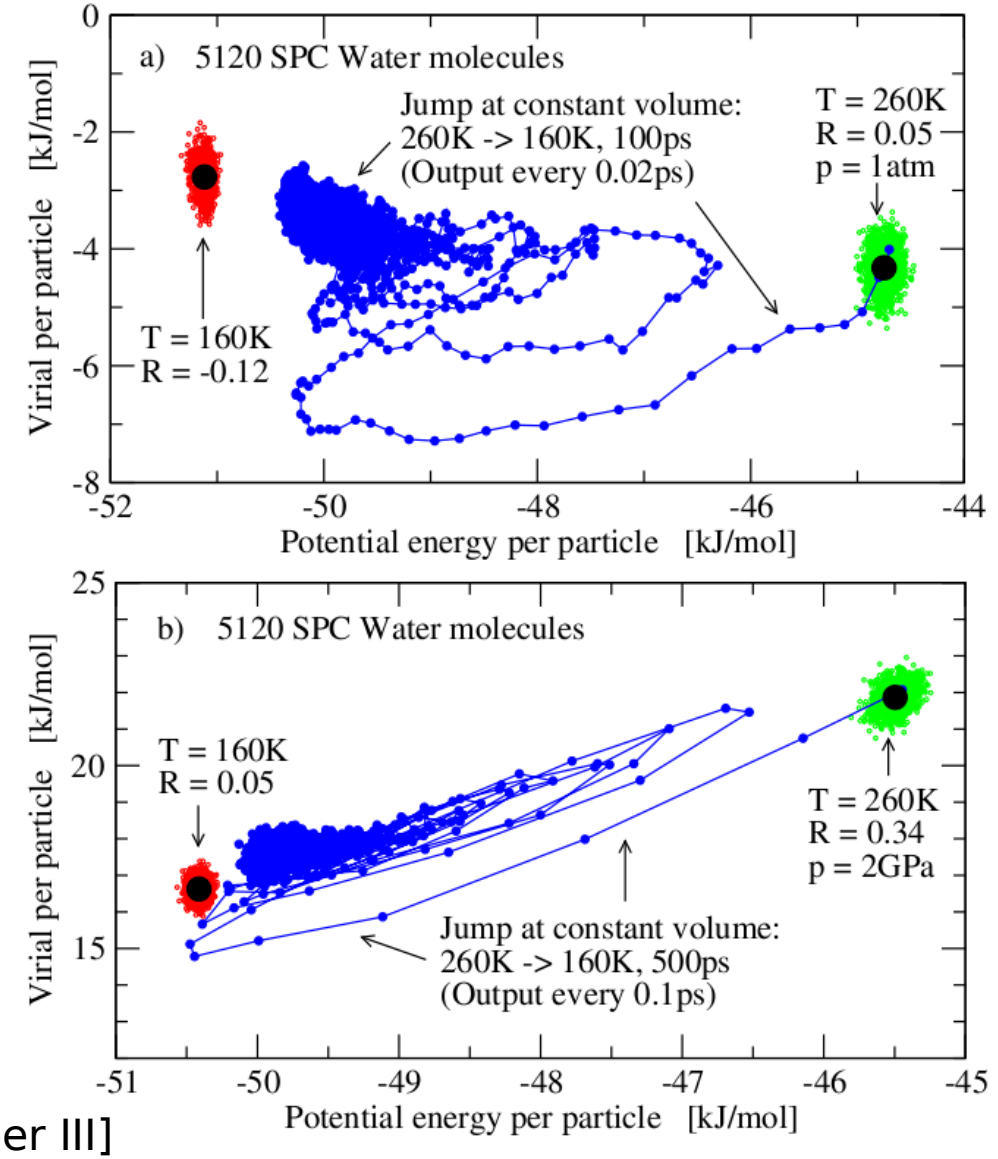
Supercritical argon [NIST database]:



Aging at constant volume is simple in SCL:

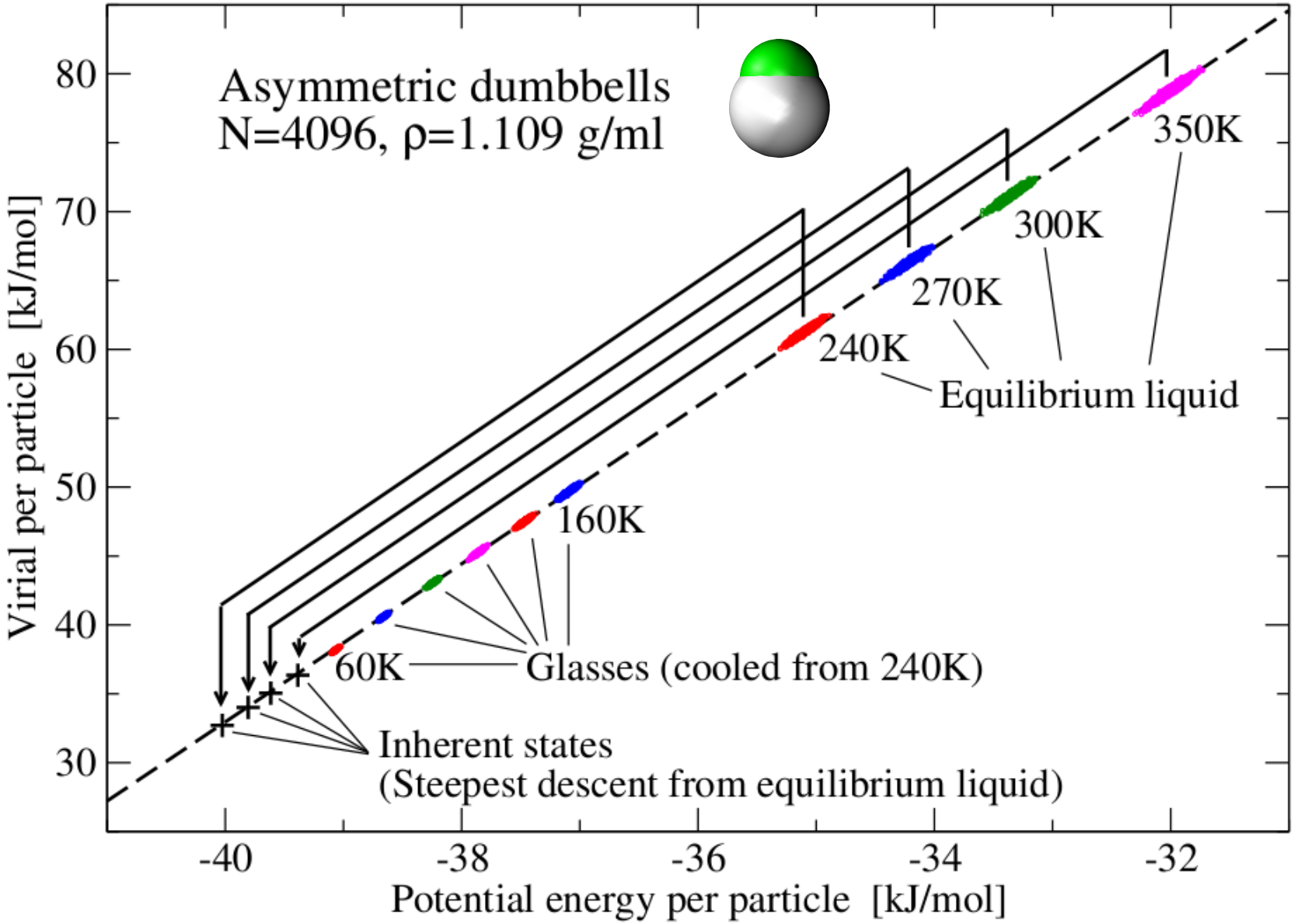


Not strongly correlating:

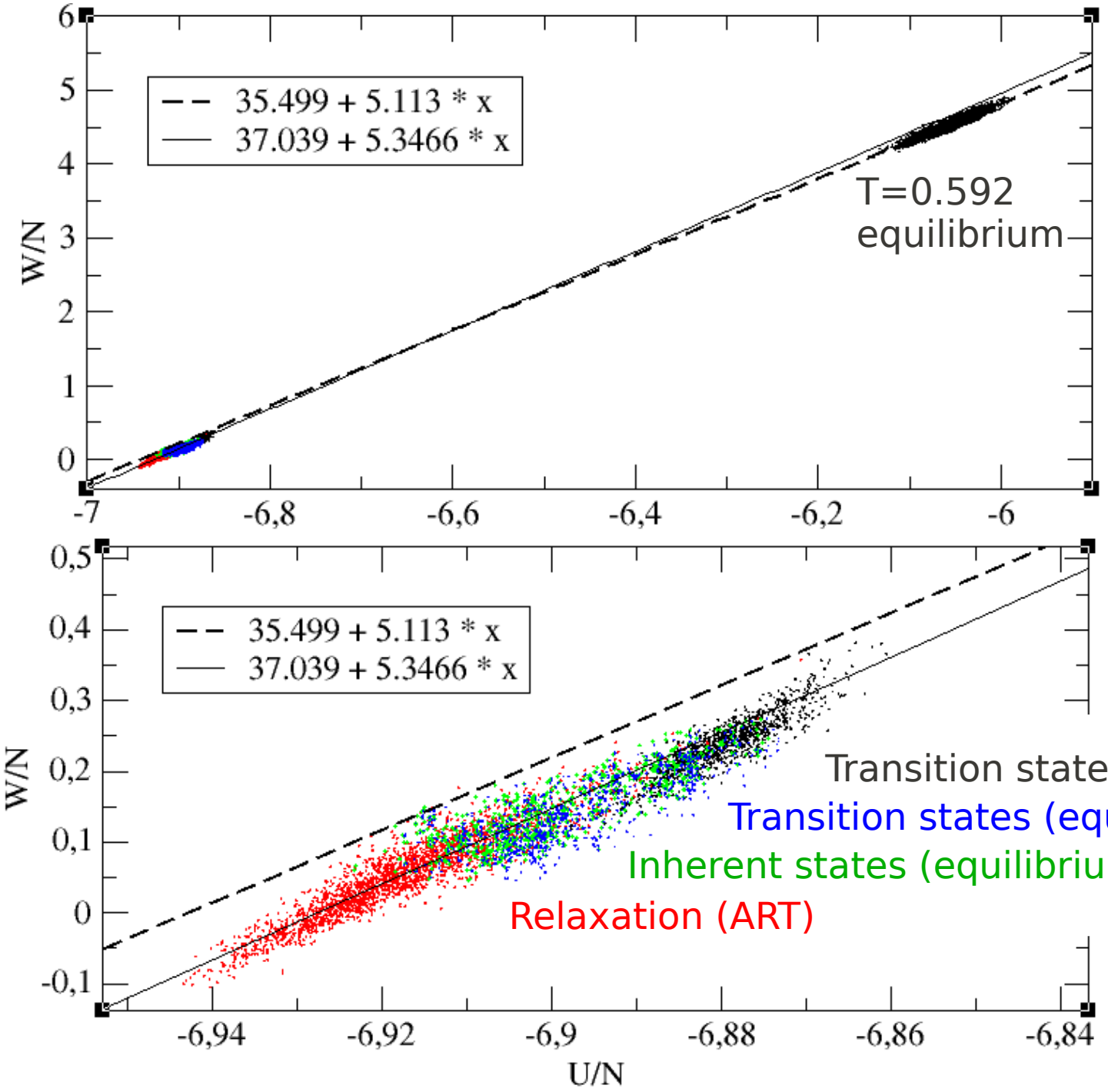


Schrøder et al., JCP 131, 234503(2009), paper III]

Strong W-U correlation is a feature of the potential energy surface



[Schrøder et al., JCP 131, 234503(2009), paper III]

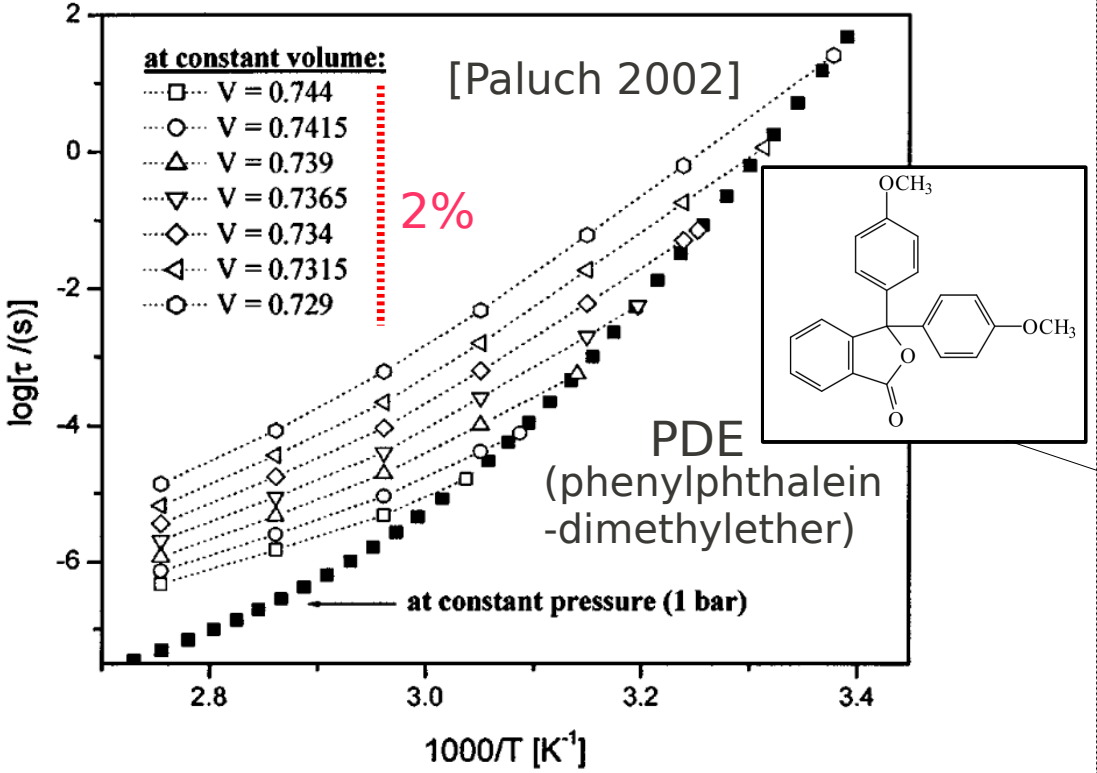


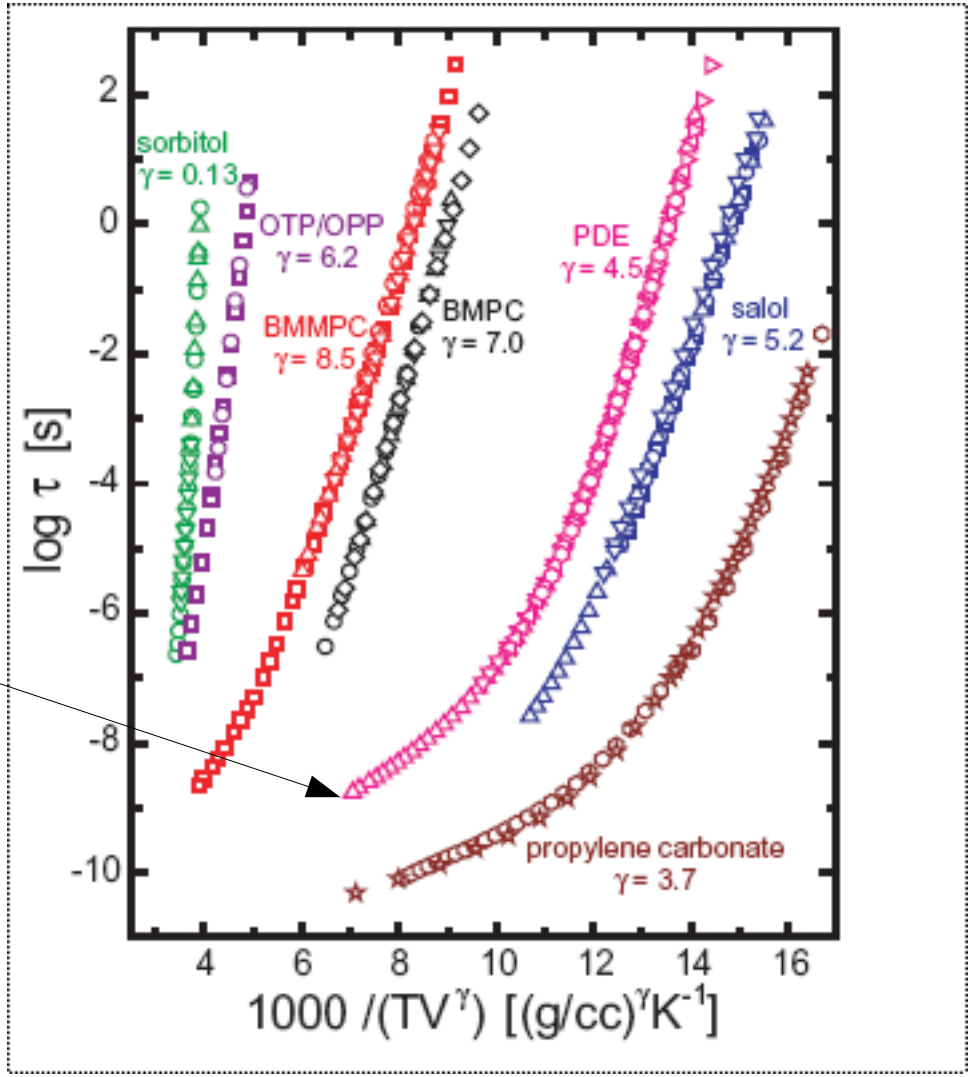
Wahnstrom BLJ

Results from a very recent collaboration [Rodney & Schrøder, KITP, 2010]

Experimental observation: Density scaling

[Tölle, Rep. Prog. Phys., 2001]
[Dreyfus et al., Phys. Rev., 2003]
[Alba-Simionesco et al., Europhys. Lett., 2004]
[Roland et al., Rep. Prog. Phys., 2005]





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

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

[Roland et al., 2005]

Hidden scale invariance:

- strongly correlating liquids obey density scaling,
- scaling exponent can be estimated from equilibrium fluctuation

[Schrøder et al., PRE 80, 041502 (2009)]
[Coslovich & Roland, JCP 130, 014508 (2009)]

Response functions proportional:

Strong correlations +
Separation of time scale +
Fluctuation-Dissipation theorem:

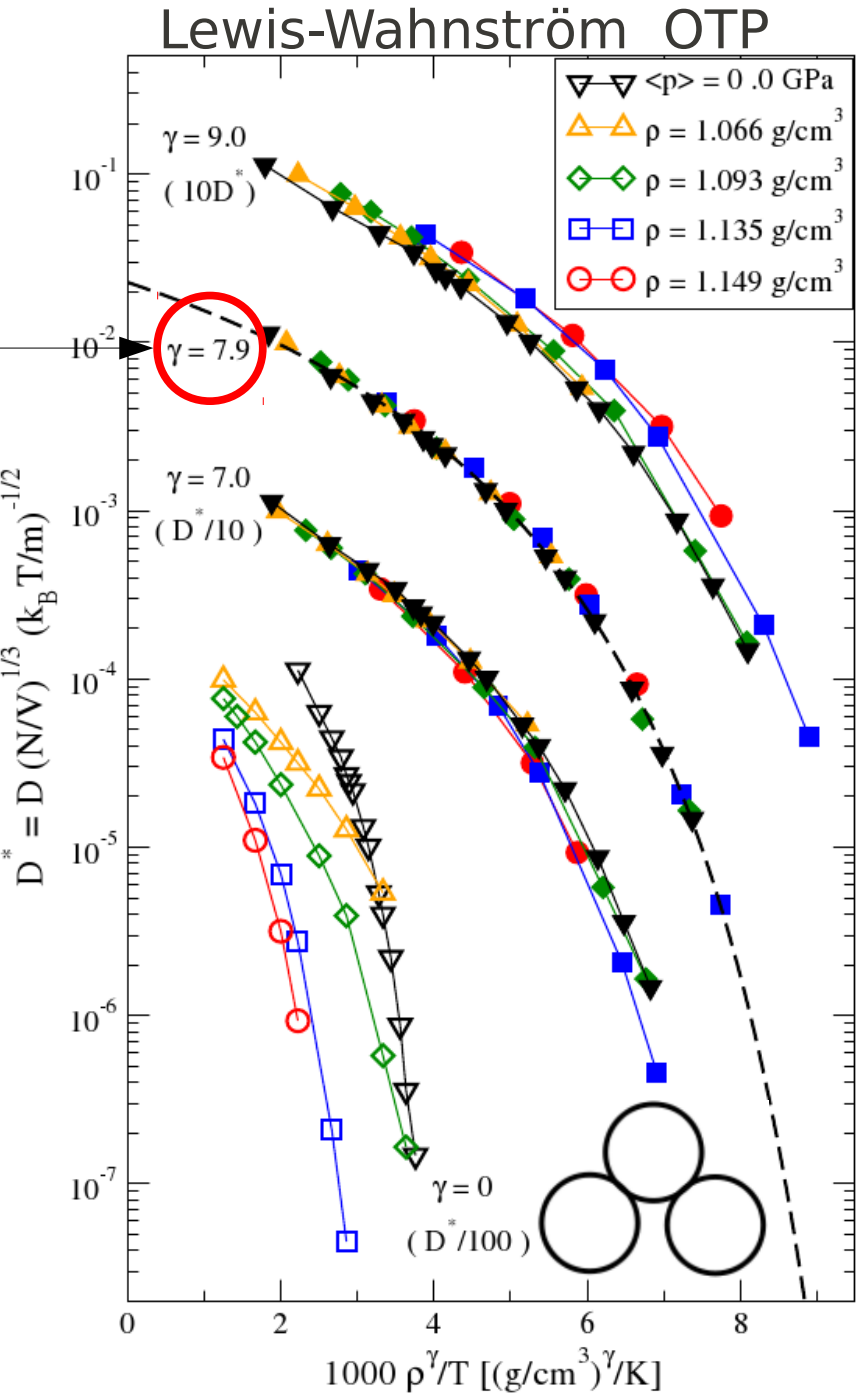
$$-Tc_V''(\omega) = \gamma^2 K_T''(\omega) = -\gamma T\beta_V''(\omega)$$

$$-T\Delta c_V = \gamma^2 \Delta K_T = -\gamma T \Delta \beta_V$$

[Ellegaard et al., JCP 126, 074502 (2007)]
[Pedersen et al., PRE 77, 011201 (2008)]

The scaling exponent can be found from linear response:

Ongoing work



A new theoretical concept: “Isomorphs”

Two state points: $(\rho_1,\ T_1)$ and $(\rho_2,\ T_2)$

Considering pairs of micro-states related by:

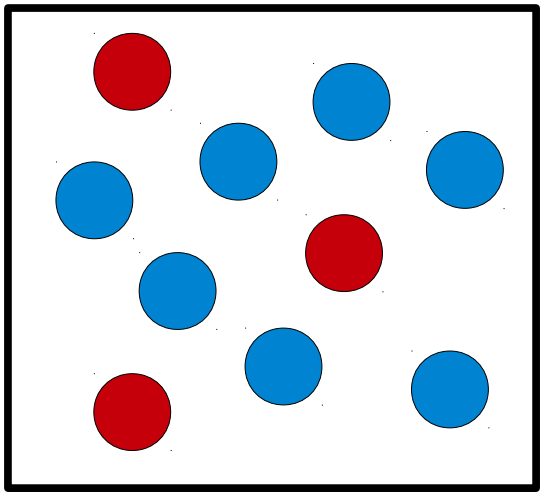
$$\vec{R}^{(2)} = (\rho_1/\rho_2)^{1/3}\,\vec{R}^{(1)}$$

State points are <u>isomorphic</u> if all “physically relavant” pairs of micro-states have proportional Boltzmann factors:

$$\exp(-U(\vec{R}^{(2)})/kT_2) = C_{12}\exp(-U(\vec{R}^{(1)})/kT_1)$$

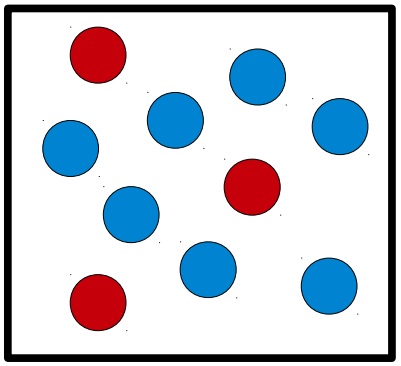
Exact for IPL, with $\dfrac{\rho_1^{n/3}}{T_1} = \dfrac{\rho_2^{n/3}}{T_2}$ giving $C_{12} = 1$

$(\rho_1,\ T_1)$



3N dim. vector in reduced units:

$$\tilde{R} = \rho_2^{1/3}\vec{R}^{(2)} = \rho_1^{1/3}\vec{R}^{(1)}$$



$(\rho_2,\ T_2)$

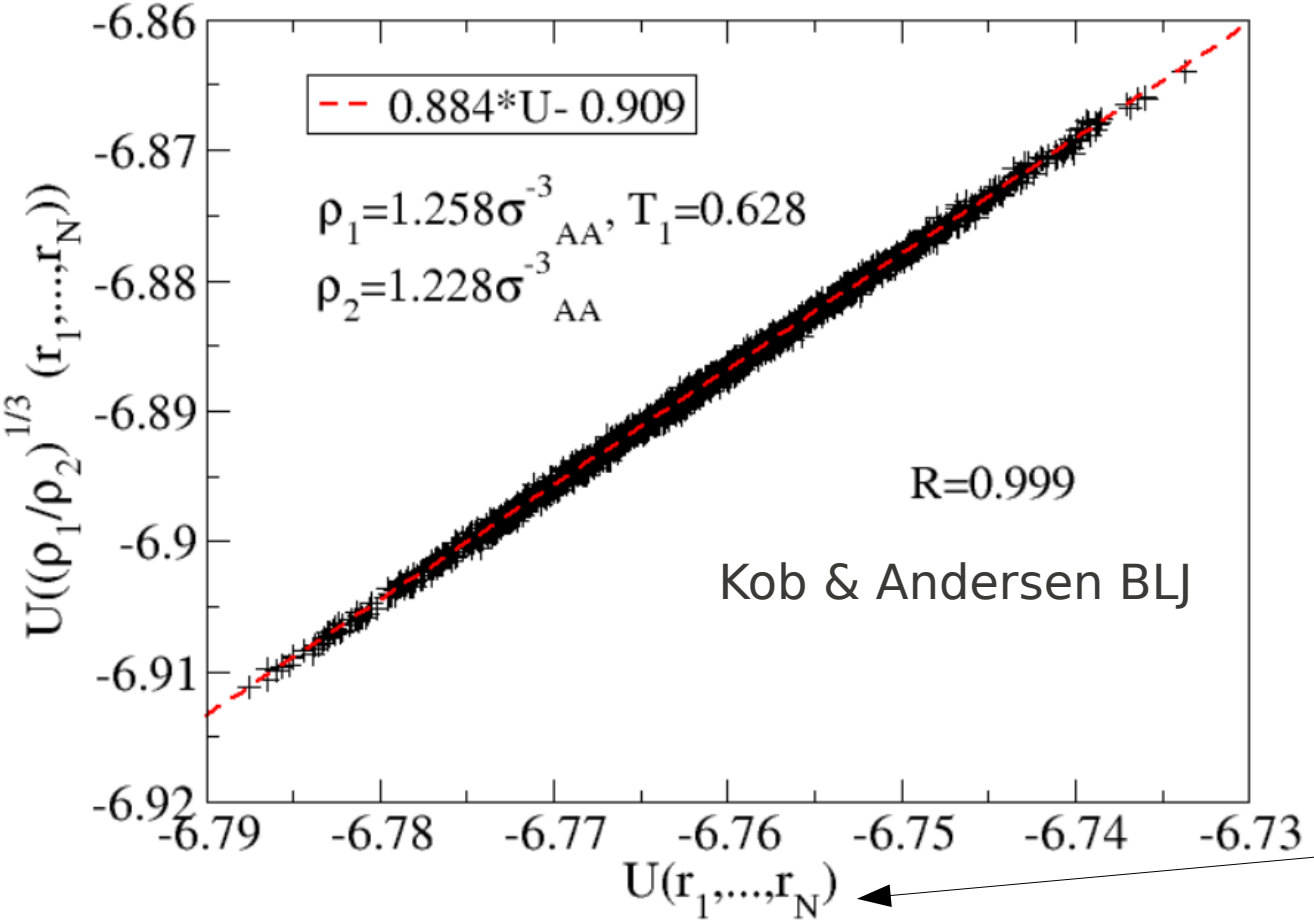
[Gnan et al., JCP 131, 234504 (2009), paper IV]

Direct Isomorph test

$$\exp\left(-U\left(\vec{R}^{(2)}\right)/kT_2\right)=C_{12}\exp\left(-U\left(\vec{R}^{(1)}\right)/kT_1\right)$$

$$\downarrow$$

$$U\left(\vec{R}^{(2)}\right)=\frac{T_2}{T_1}U\left(\vec{R}^{(1)}\right)-kT_2\ln\left(C_{12}\right)$$



$$\vec{R}^{(2)}=\left(\rho_1/\rho_2\right)^{1/3}\vec{R}^{(1)}$$

Slope tells us what the new temperature should be:

$$T_2=0.884\,T_1=0.555$$

$$\left(C_{12}\neq 1\right)$$

Configurations taken from equilibrium simulation at (ρ_1, T_1)

[Gnan et al., JCP 131, 234504 (2009), paper IV]

A new theoretical concept: “Isomorphs”

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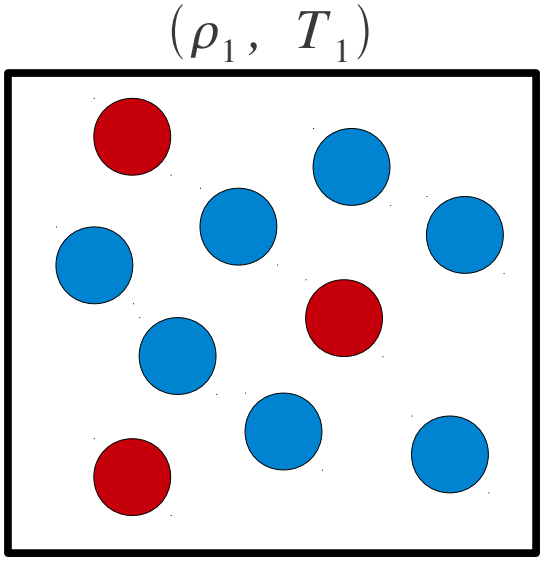
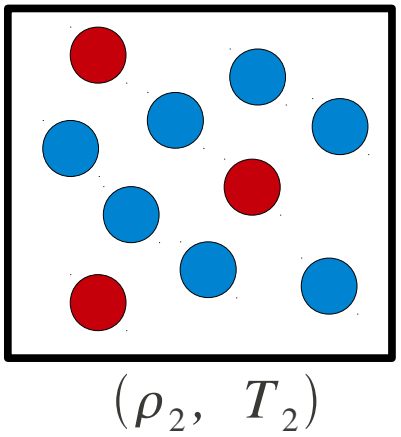


3N dim. vector in reduced units:

$$\tilde{R} = \rho_2^{1/3}\vec{R}^{(2)} = \rho_1^{1/3}\vec{R}^{(1)}$$

From this assumption follows a number of properties:

- Invariant on an isomorphic curves in state diagram:
  - Excess entropy, $S_{ex} = S - S_{ideal}$.
  - Structure (in reduced units, $\tilde{\mathbf{r}}_i \equiv \rho^{1/3}\mathbf{r}_i$).
  - Dynamics (in reduced units, $\tilde{t} = t\rho^{1/3}\sqrt{kT/m}$), including high-order correlation functions.
- W(t) and U(t) are strongly correlated.
- Isochores are straight lines in W,U-plot.



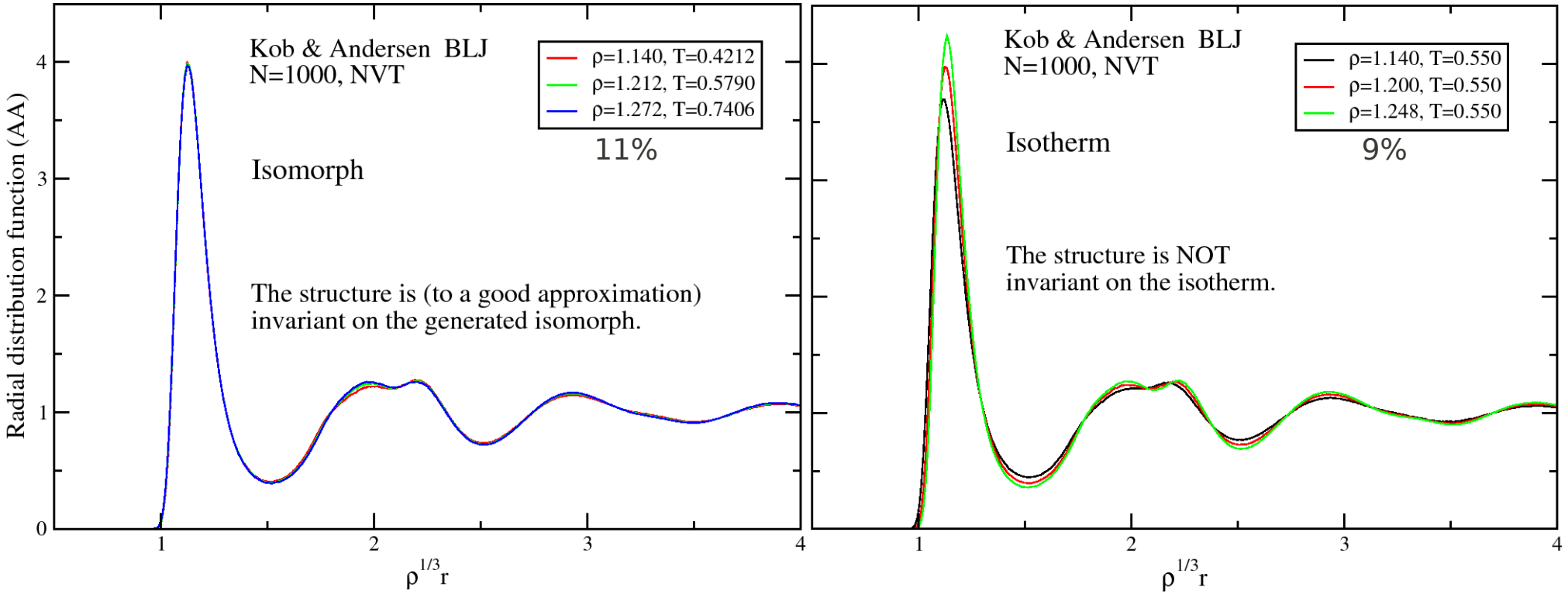
[Gnan et al., JCP 131, 234504 (2009), paper IV]

Test by MD simulations:

Generate state points with invariant excess entropy:

$$\gamma \equiv \left(\frac{\partial \ln(T)}{\partial \ln(\rho)}\right)_{S_{ex}} = \frac{\langle \Delta U \Delta W \rangle}{\langle (\Delta U)^2 \rangle} = \left(\frac{\partial W}{\partial U}\right)_V$$

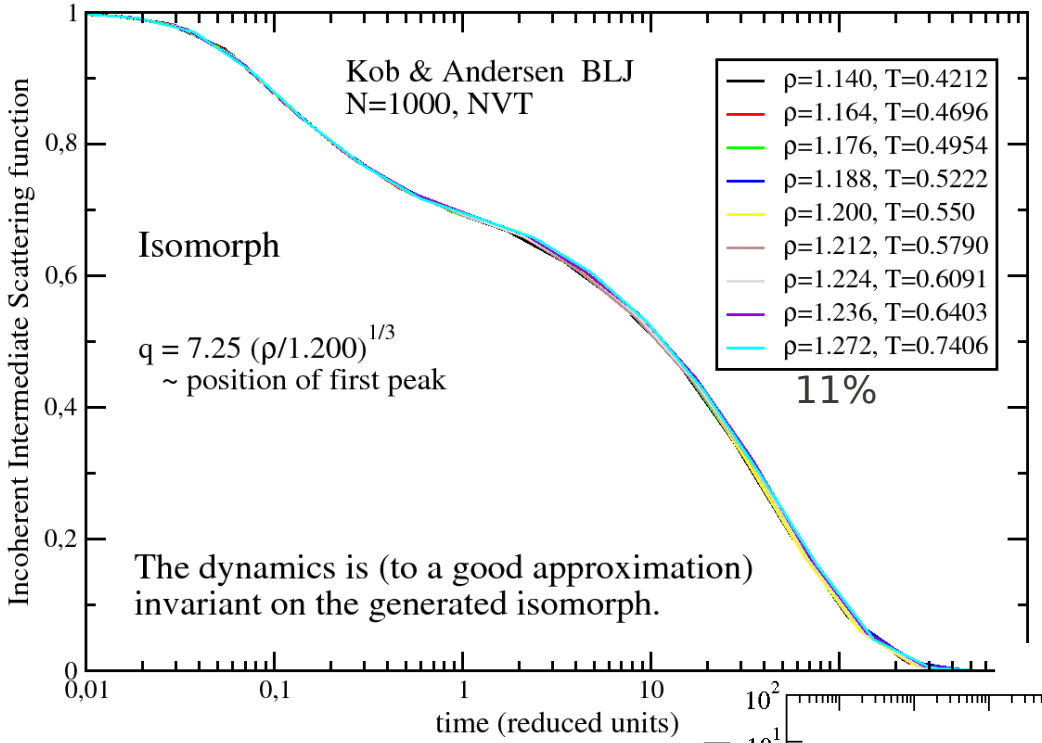
... and then check if the other invariants follow...

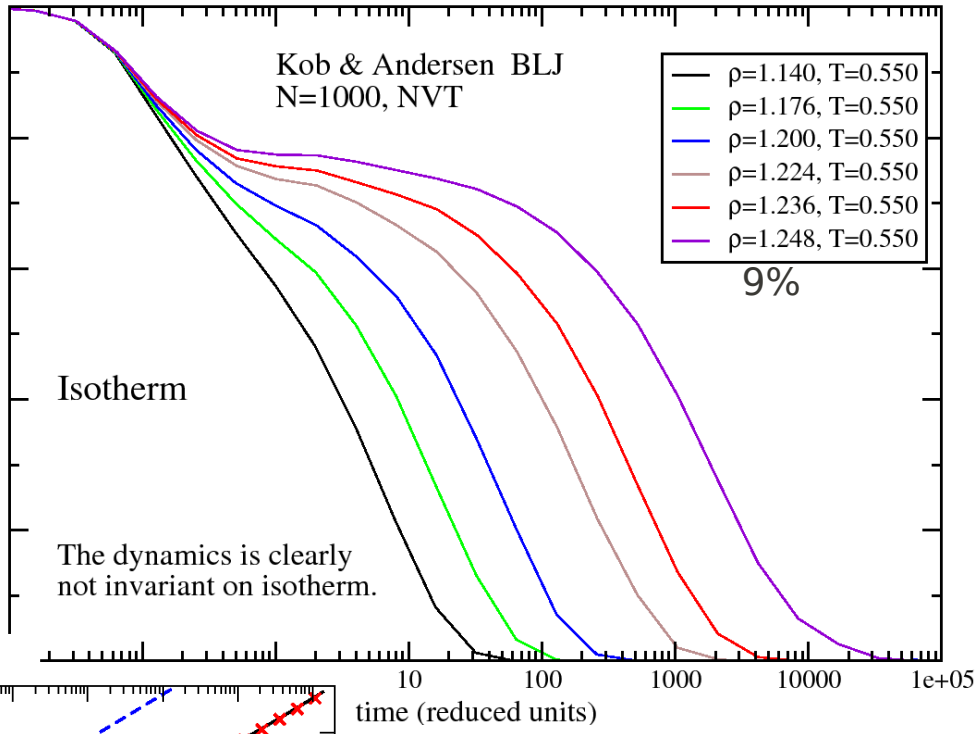


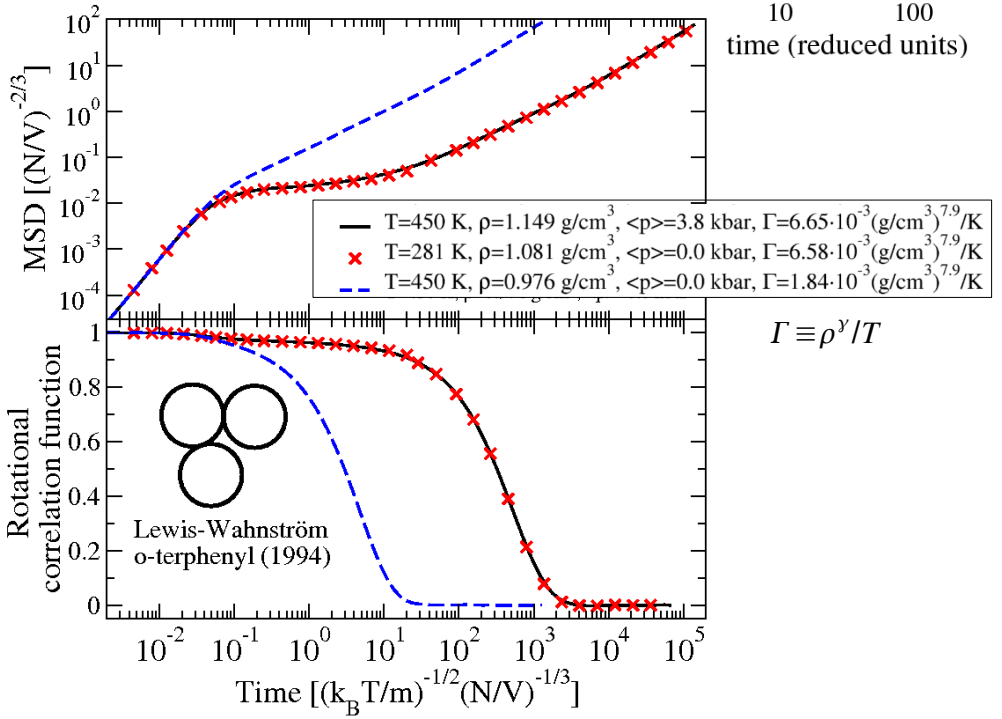
Structure is (to a good approximation) invariant on isomorph.

[Gnan et al., JCP 131, 234504 (2009), paper IV]

Dynamics is (to a good approximation) invariant on isomorph.



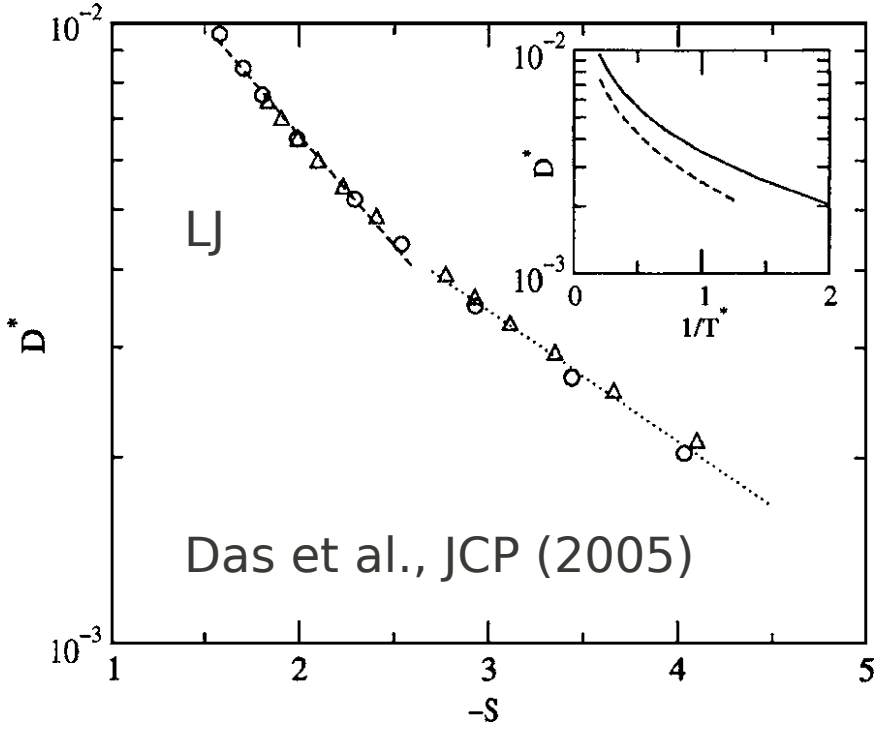


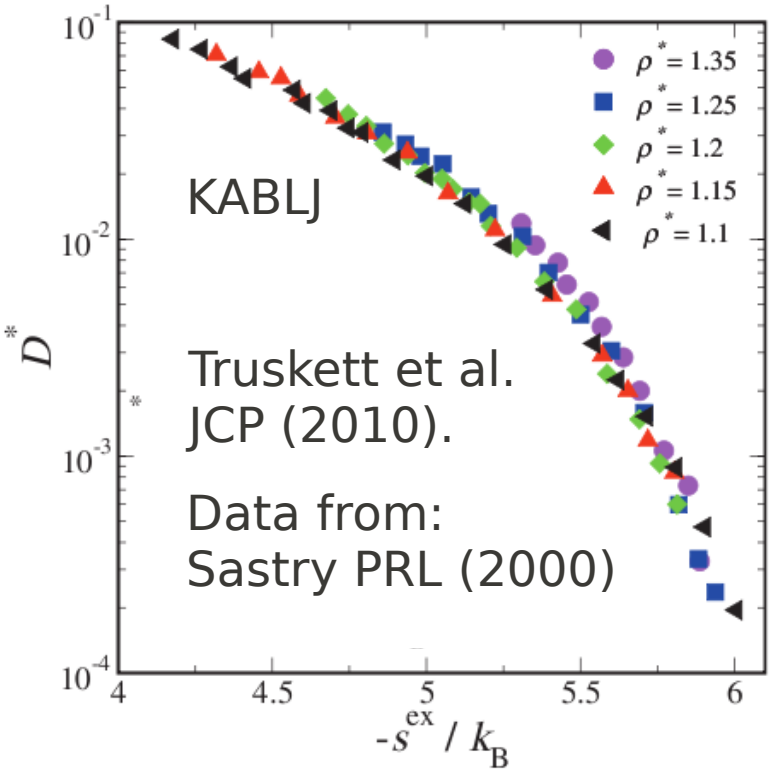


$\Gamma \equiv \rho^{\gamma}/T$

From talk by Charusita Chakravarty: Failure of Rosenfeld scaling

$$\tilde{D} \sim \exp(S_{ex})$$

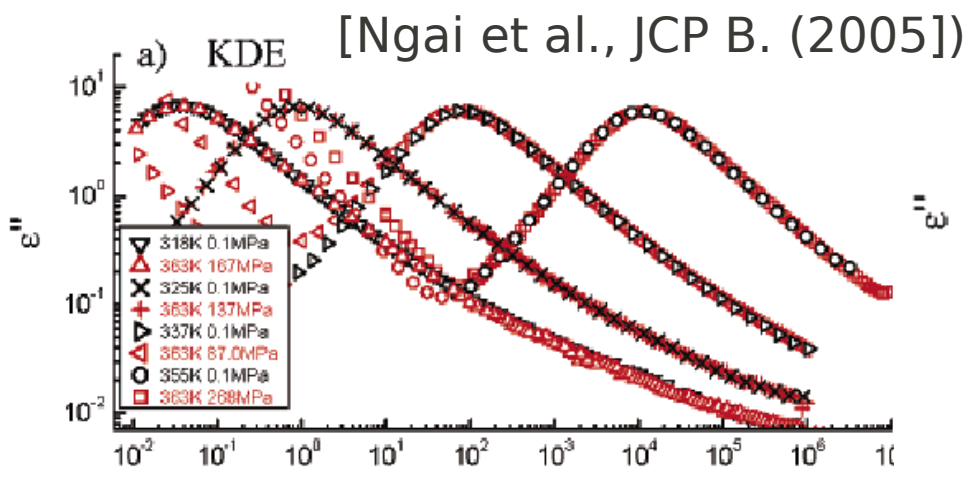


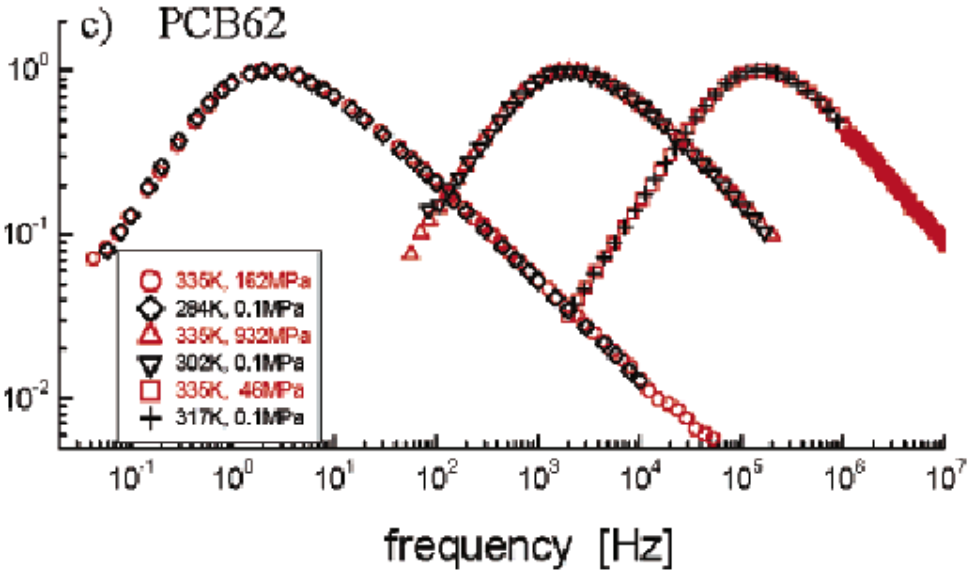


But succes for: $\tilde{D} \sim f(S_{ex})$

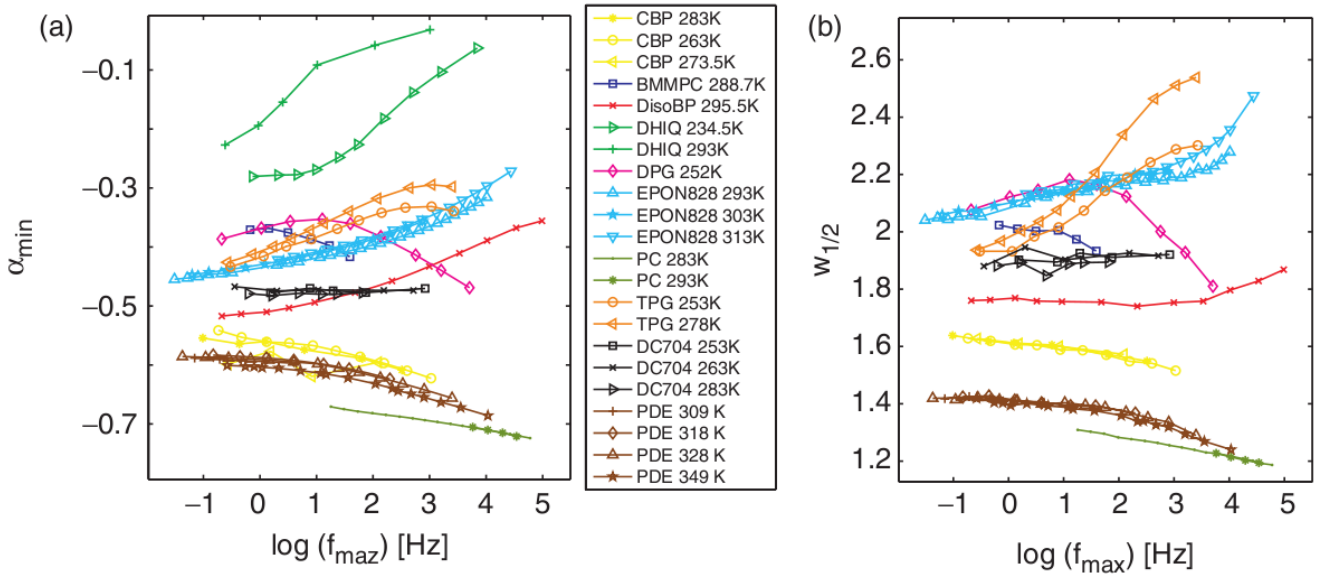
Experimental observation: Isochronal superposition

[Ngai et al., JCP B. (2005])

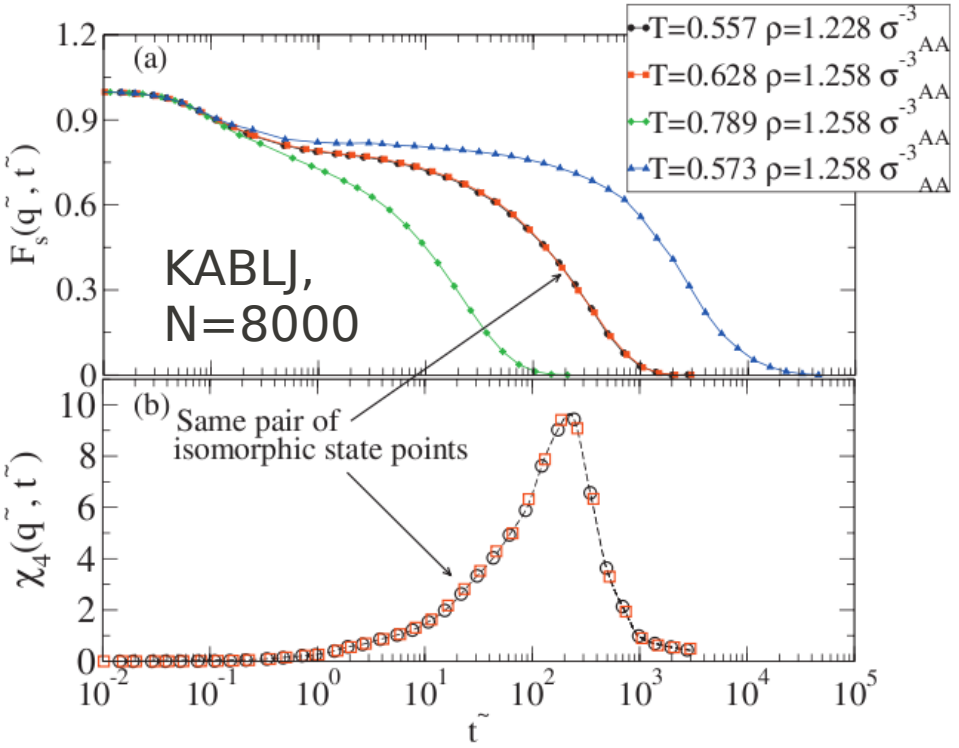




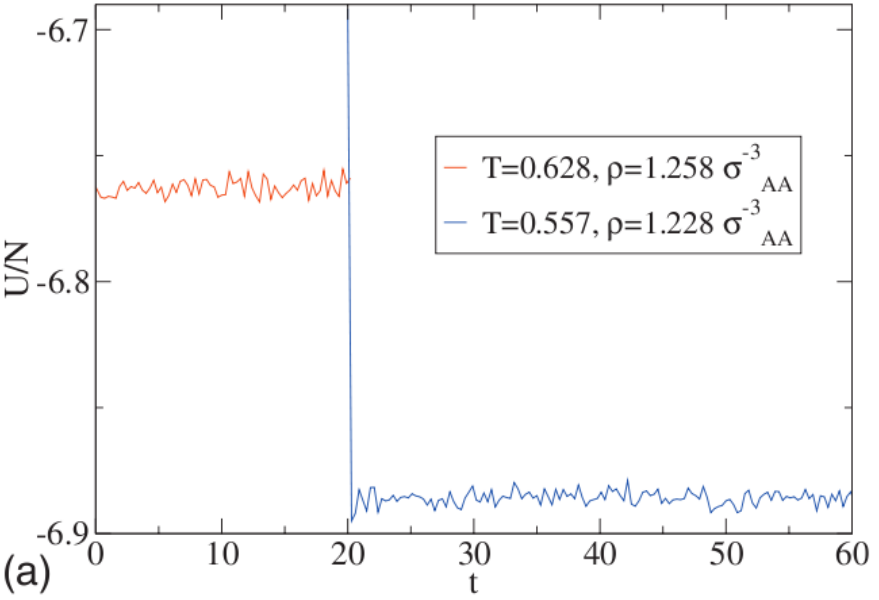
Shape parameters as Function of relaxation time:

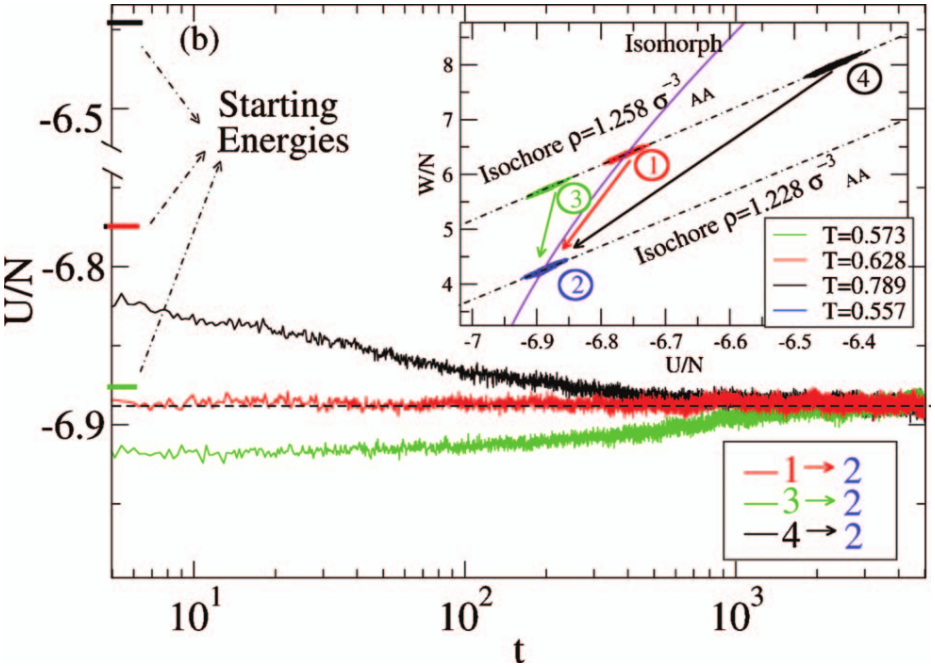


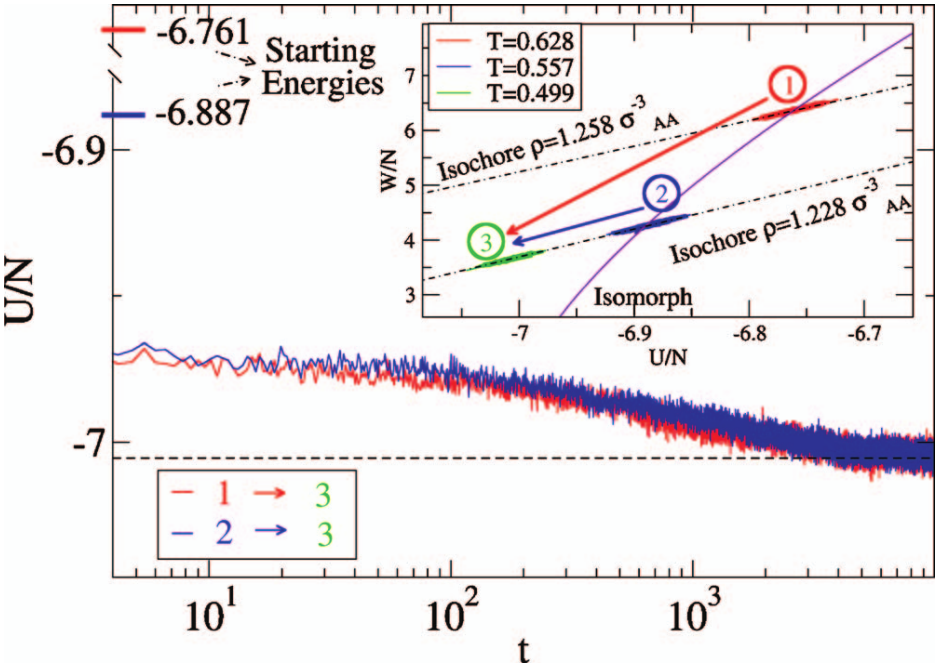
[Nielsen, Pawlus, Paluch, and Dyre, Phil. Mag. (2008)]



Jumps between isomorphic state points are instantaneous!

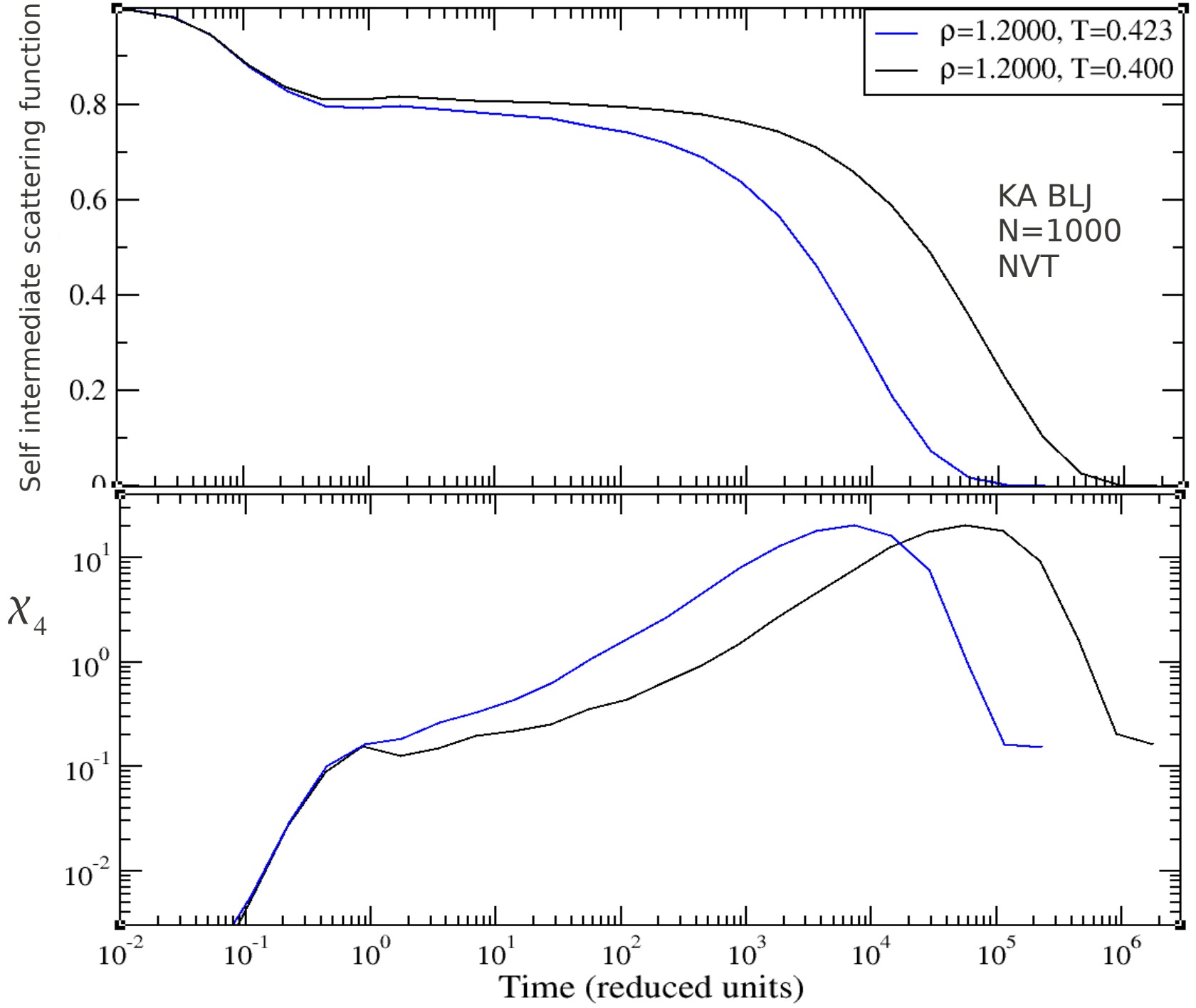




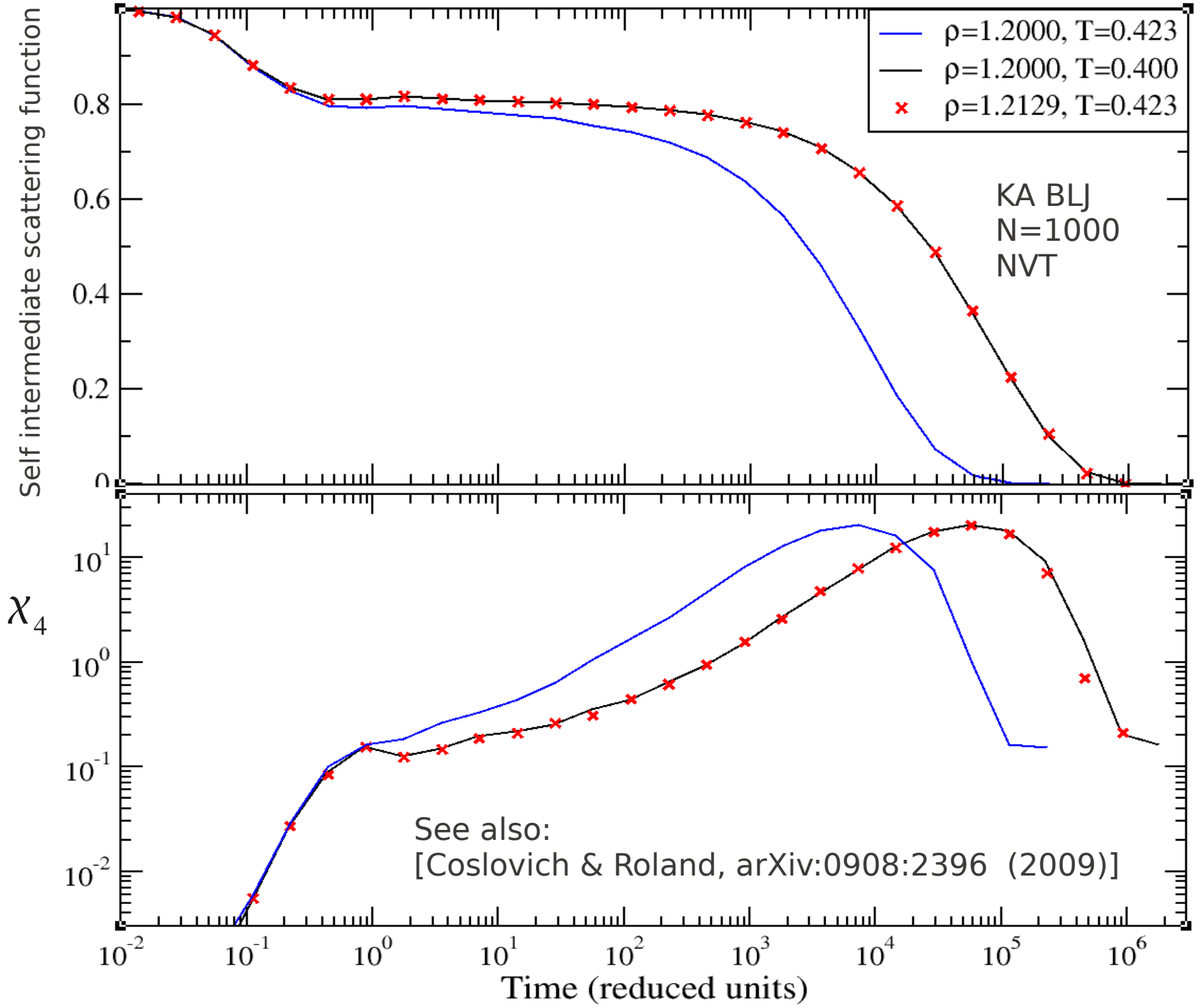


[Gnan et al., JCP 131, 234504 (2009), paper IV; Gnan et al. PRL (2010)]

Towards low temperatures:



Towards low temperatures:

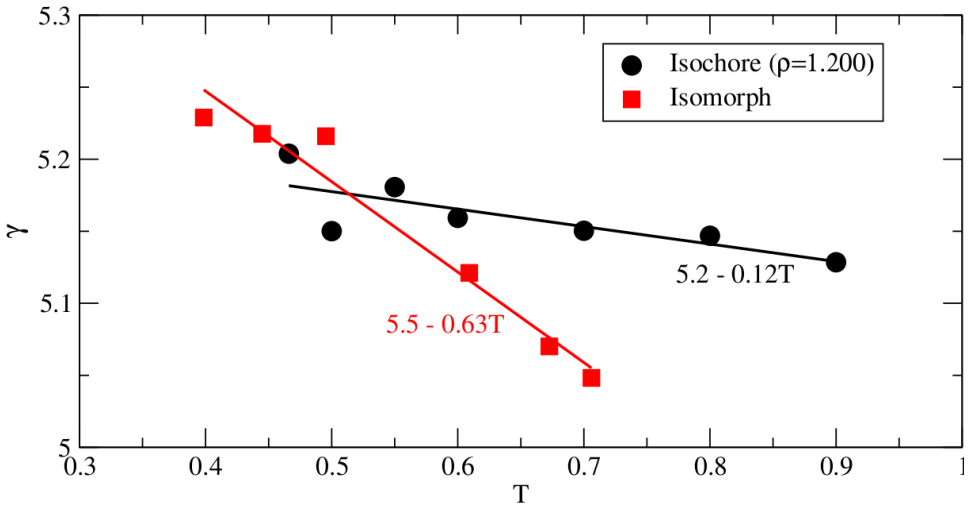


Isochores are straight lines in the W,U state diagram - a consequence of the existence of isomorphs.

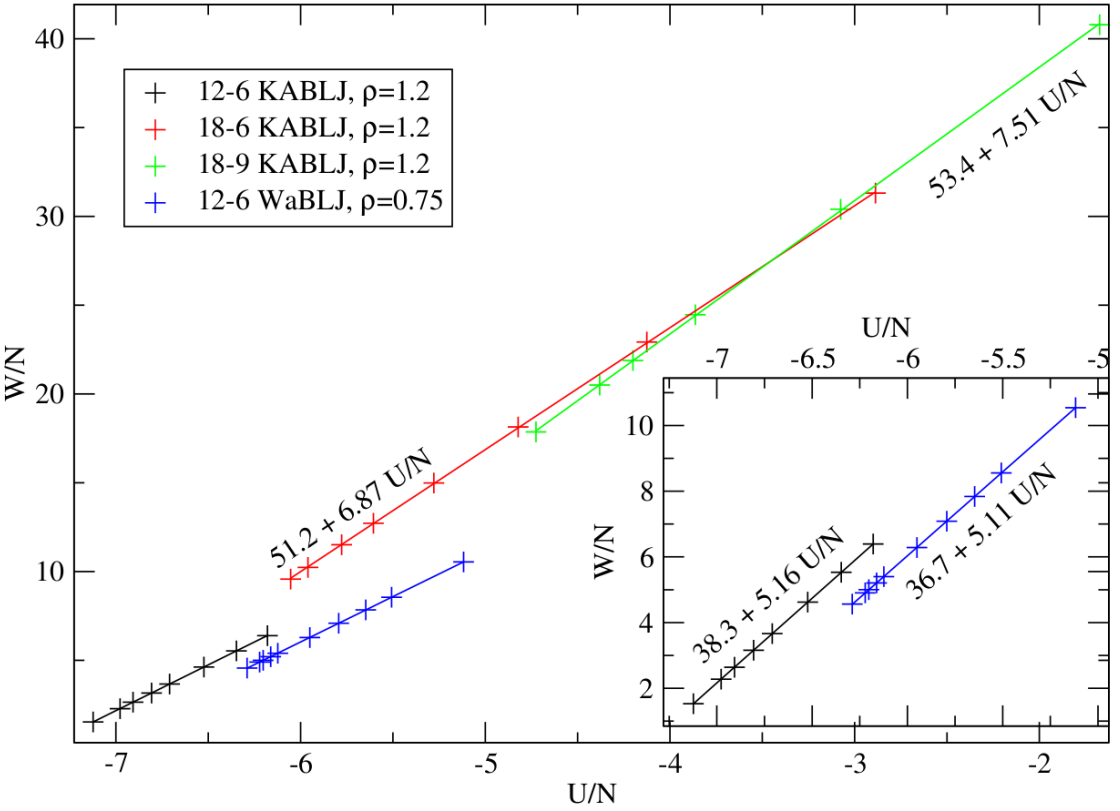
Isomorphic prediction:

$$\gamma \equiv \left(\frac{\partial \ln(T)}{\partial \ln(\rho)}\right)_{S_{ex}} = \frac{\langle \Delta U \Delta W \rangle}{\langle (\Delta U)^2 \rangle} = \left(\frac{\partial W}{\partial U}\right)_V$$

is constant on an isochore.



Isochores in generalized LJ systems:



[Schrøder et al., arXiv:1004.5145 (2010), paper V]

RUMD.org

MD on GPU

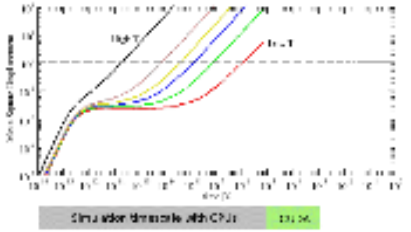
Roskilde University Molecular Dynamics with GPUs

Hoire Larson, Thomas B. Schrøder, Nicholas P. Bailey, Trond Ingebrigtsen, Nicoletta Gnan, Lasse Jelling, Jesper Schmidt Hansen

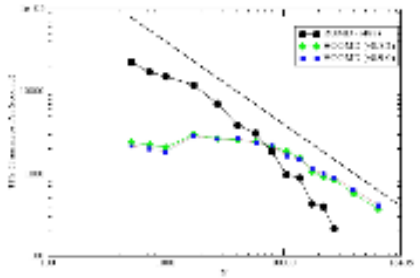
DNRF Centre "Glass and Time", IMFUFA, Department of Sciences, Roskilde University, Denmark

The Need for Speed

- We want to test theories and investigate new phenomena
- We want to simulate on the millisecond timescale and higher
- Simulations will reach the timescales of measurents on real liquids and glasses



RUMD and HOOMD compared



- RUMD has good scaling for small systems (< 10000 particles)

RUMD features

MD parameters

- NVE, NVT with Nose-Hoover thermostat, NPT with constraints (fixed bonds)
- Monoatomic, Kob Andersen (binary LJ)
- Pair potentials: LJ(12,6), LJ(m,n), IPL(18), IPL(n), ...

Trajectory storage

- Configurations are stored in compressed XYZ format
- Trajectories are saved in blocks with varying interval between configurations
- Allows study of very long time-series with limited storage
- Tools for calculating basic statistics, MSD, RDF (also during simulation)

Optimization, performance and usability

- Focus on small samples of 1000 – 10000 particles
- Speedup compared to best CPU based programs: factor 20 expected
- Easy access to main loop for doing experiments
- Easy way to add new potentials

Technical details and Availability

- Source code in C++– with CUDA extensions
- Most code in a library and linked from small common or user-provided main programs
- Tests for guarding performance and consistency with tweaking of GPU scheduling parameters
- Tests for expected physics (energy conservation, thermostat performance, momentum control,...)
- Current code-size: 9650, 3803 lines
- Source-code will be covered by a free license
- Soon to be announced on http://glass.ruc.dk and http://rumd.org

What is the shape of isomorphs in the W,U-plot?

Consider a multi-component generalized Lennard-Jones potential:

$$\phi_{ij}(r_{ij}) = \phi_{ij}^{(n)}(r_{ij}) + \phi_{ij}^{(m)}(r_{ij}), \quad \phi_{ij}^{(m)}(r_{ij}) \equiv \epsilon_{ij}^{(m)} \left(\sigma_{ij}^{(m)}/r_{ij}\right)^m$$

U and W has contribution from the two IPL terms of the potential:

$$U = U_n + U_m, \quad W = \frac{n}{3}U_n + \frac{m}{3}U_m, \quad U_m \equiv \sum_{i>j} \phi_{ij}^{(m)}(r_{ij}) \qquad W \equiv -\frac{1}{3}\sum_{pairs} r\frac{\partial U(r)}{\partial r}$$

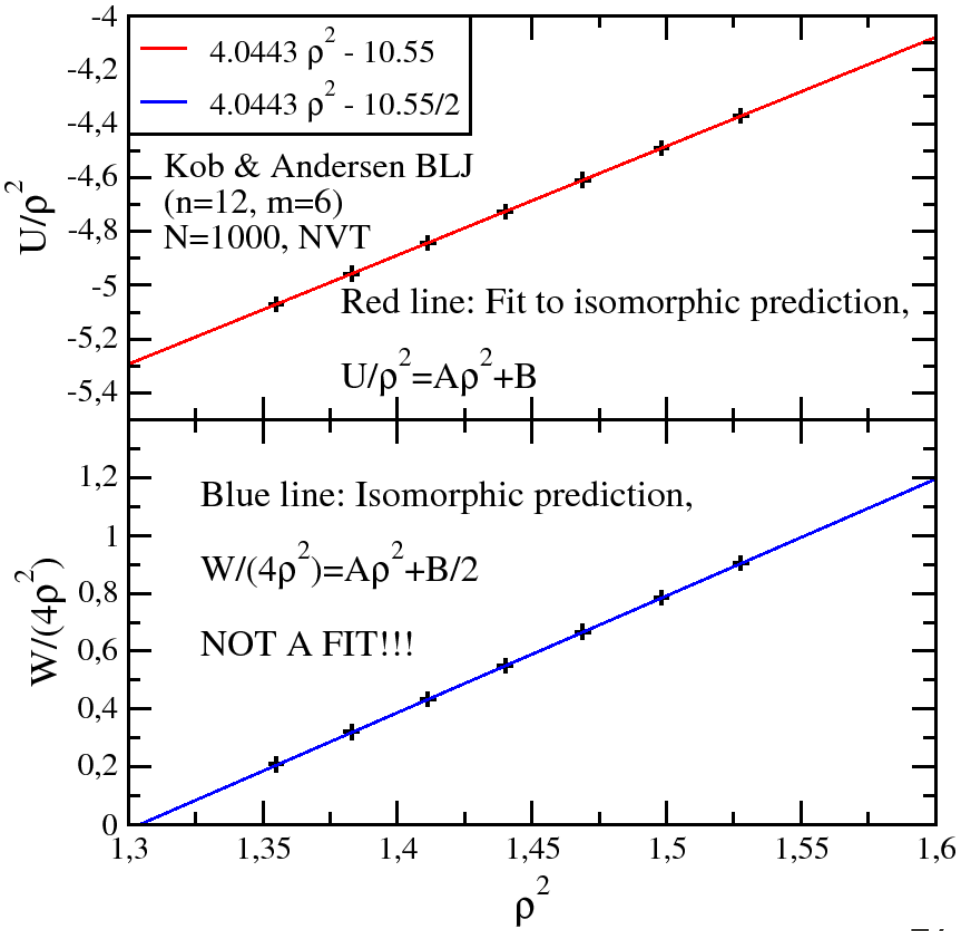
On an isomorph the two IPL terms scale trivially with density (since the structure is invariant):

$$U_m(\rho) = \left(\frac{\rho}{\rho_*}\right)^{m/3} U_{m,*}(\rho_*) = \tilde{\rho}^{m/3} U_{m,*}$$

... and we thus get:

$$U = \tilde{\rho}^{n/3} U_{n,*} + \tilde{\rho}^{m/3} U_{m,*}$$

$$W = \frac{n}{3}\tilde{\rho}^{n/3} U_{n,*} + \frac{m}{3}\tilde{\rho}^{m/3} U_{m,*}$$



Shape of isomorphs in W,U-plot only depends on exponents 'm' and 'n'.

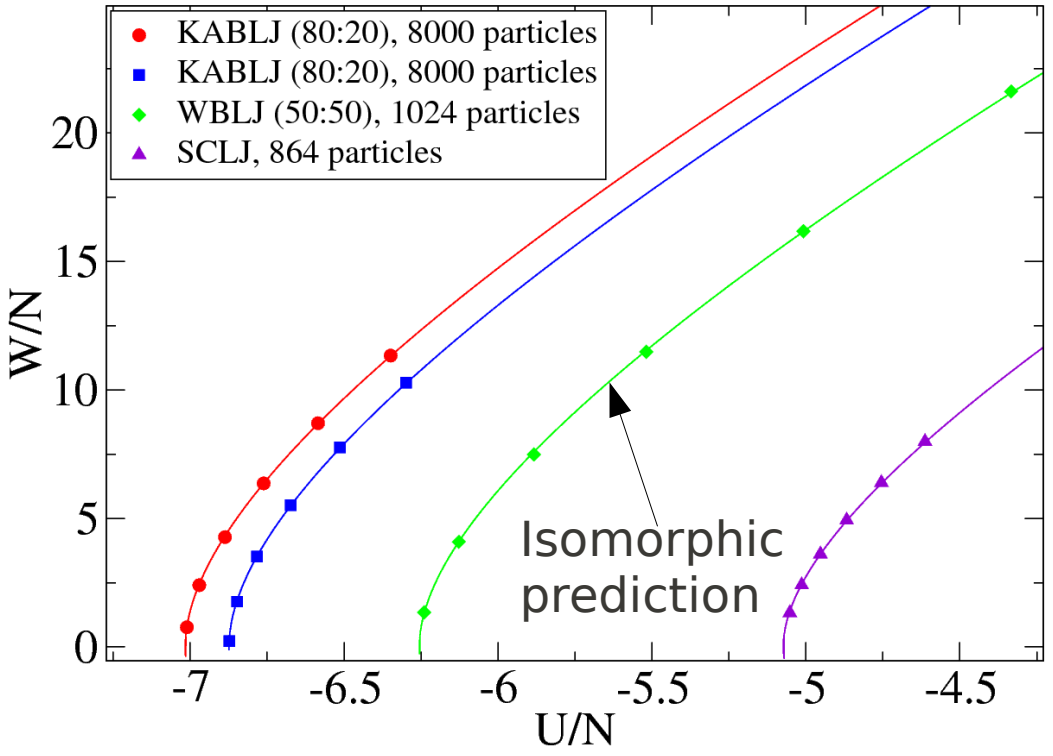
Multi-component generalized Lennard-Jones potential:

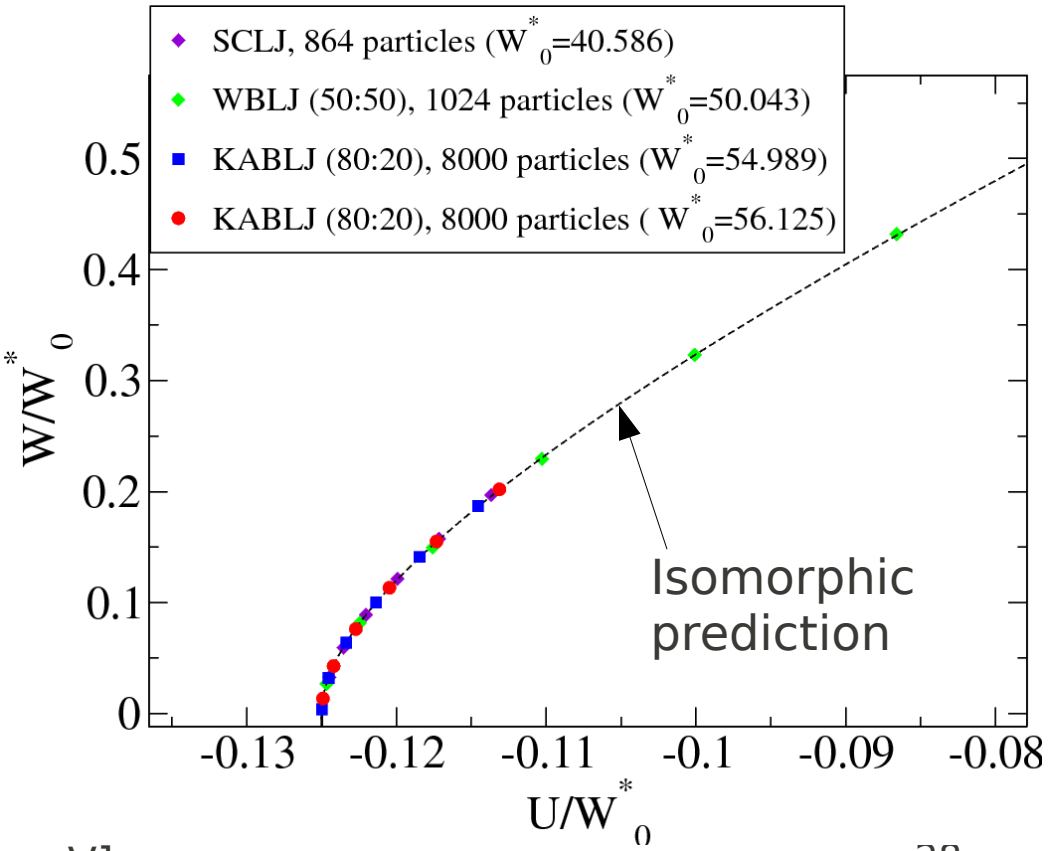
$$\phi_{ij}(r_{ij}) = \phi_{ij}^{(n)}(r_{ij}) + \phi_{ij}^{(m)}(r_{ij}), \quad \phi_{ij}^{(m)}(r_{ij}) \equiv \epsilon_{ij}^{(m)} \left(\sigma_{ij}^{(m)}/r_{ij}\right)^m$$

↓ Invariance of structure

Isomorphic prediction:

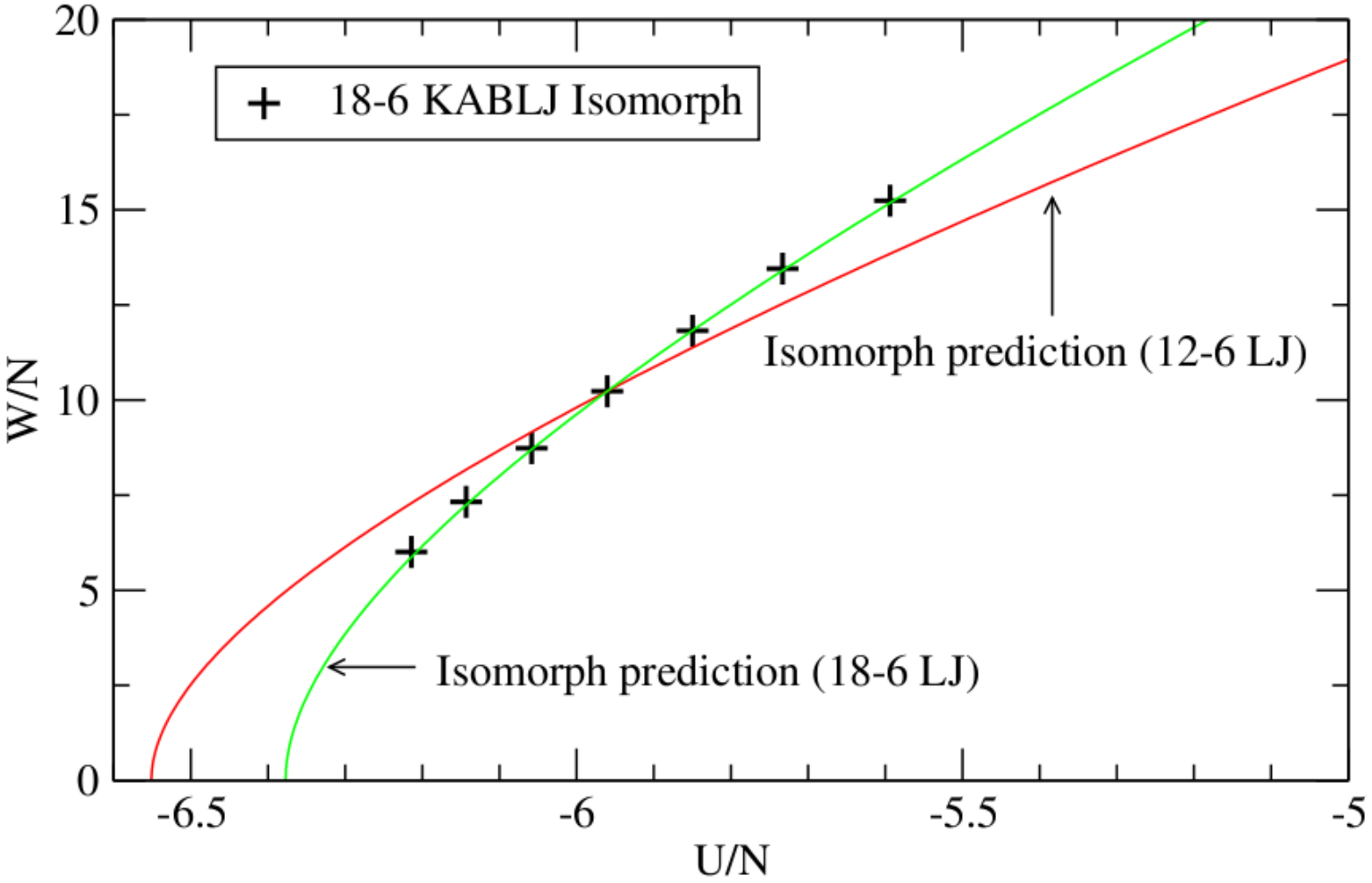
$$U = \tilde{\rho}^{n/3} U_{n,*} + \tilde{\rho}^{m/3} U_{m,*}$$
$$W = \frac{n}{3}\tilde{\rho}^{n/3} U_{n,*} + \frac{m}{3}\tilde{\rho}^{m/3} U_{m,*}$$





[Schrøder et al., arXiv:1004.5145 (2010), paper V]

m,n depence on shape of isomorphs



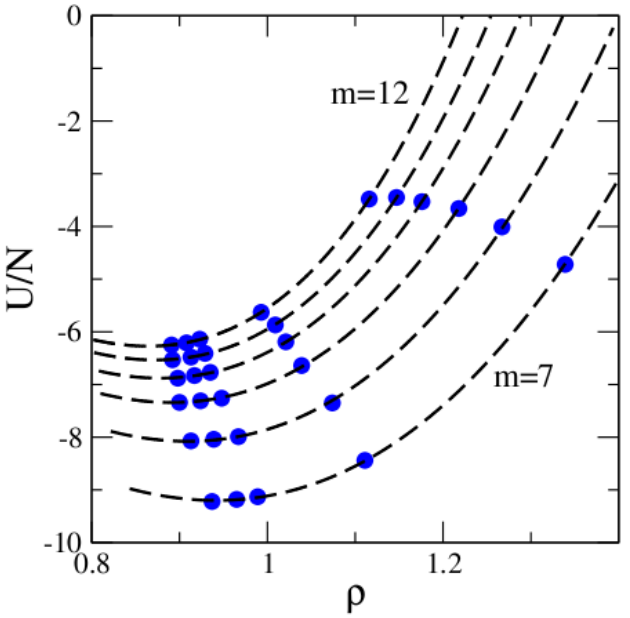
[Schrøder et al., arXiv:1004.5145 (2010), paper V]

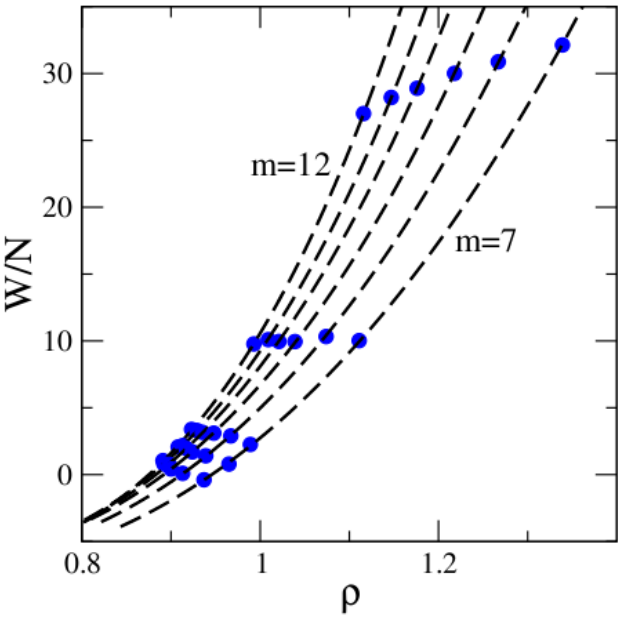
Liquid-solid coexistence, the liquid phase

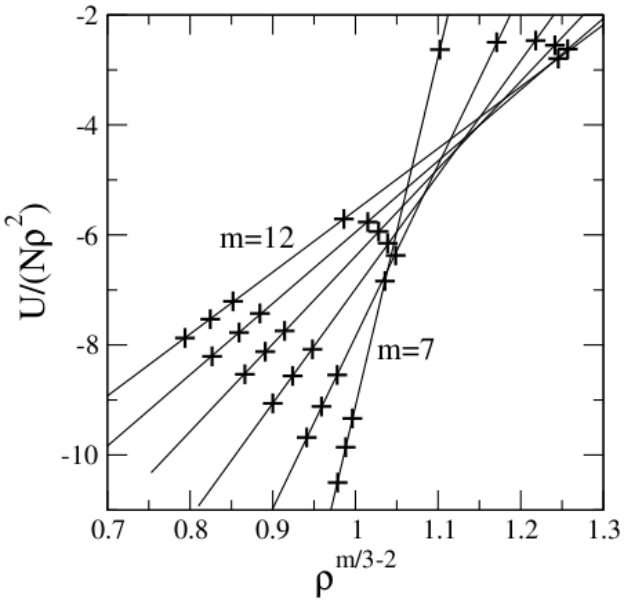
Generalized LJ,
Single Component

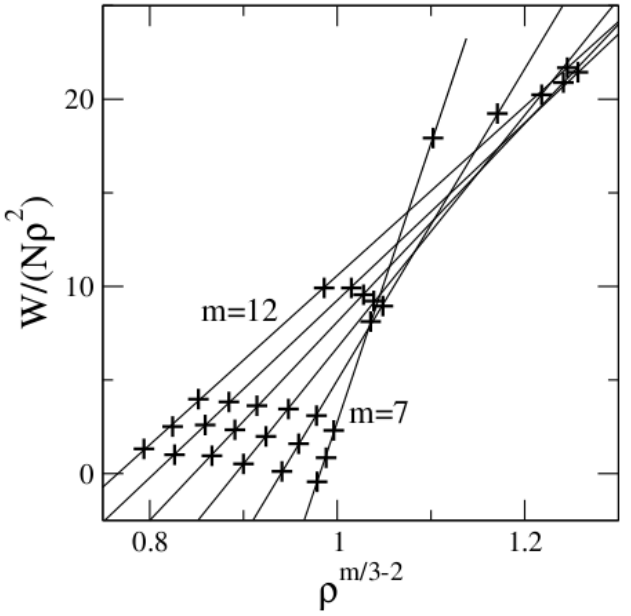
Simulation results
from Ahmed & Sadus:
[JCP 131, 174504 (2009)]

Lines:
Isomorphic prediction





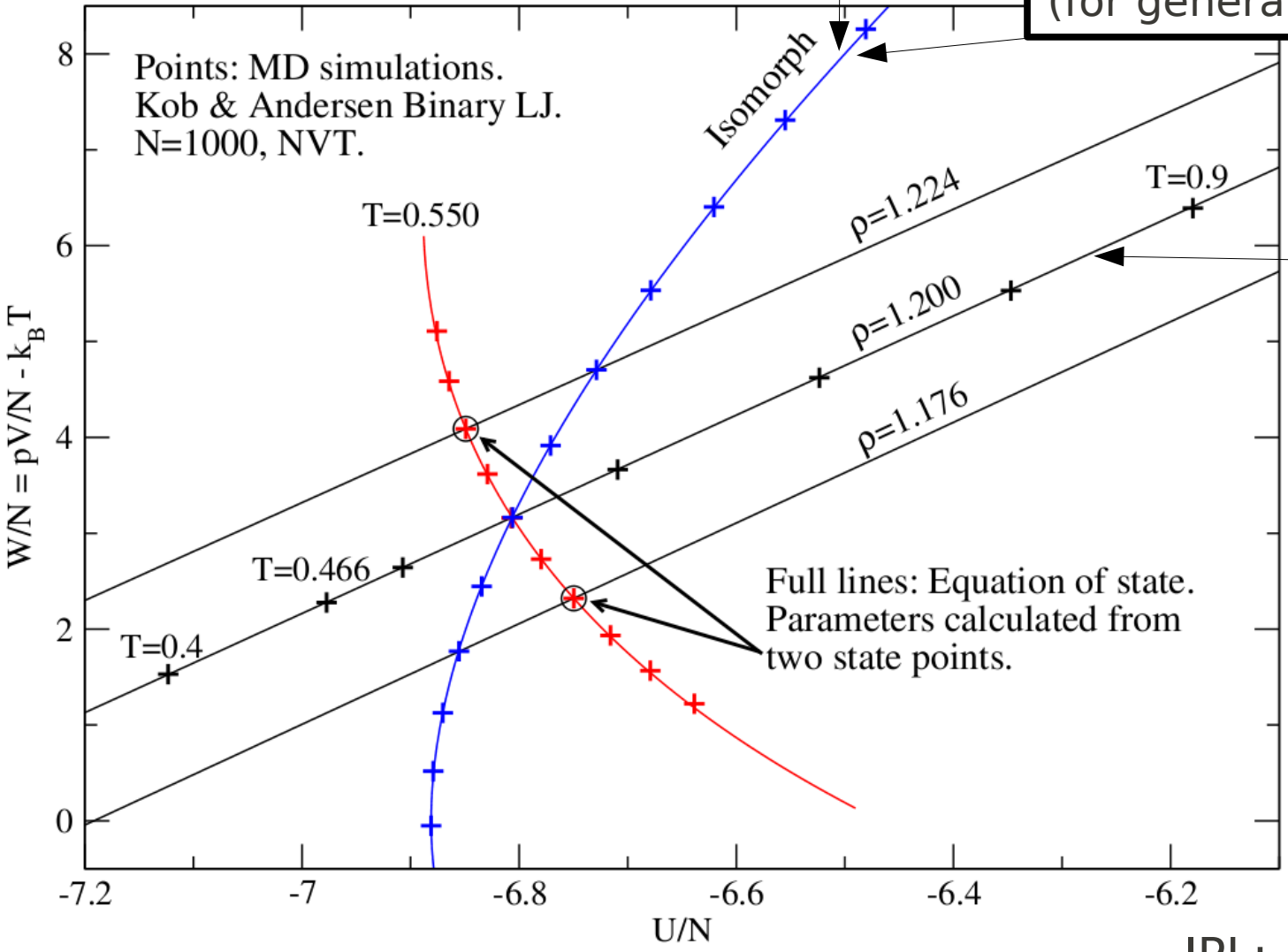




Understanding isomorphs and isochores leads to an equation of state:

$U(\rho,T) = \ldots$

$W(\rho,T) = \ldots$



Isomorph prediction:
Shape of isomorphs in U,W diagram
(for generalized LJ models)

Isomorph prediction:
$W = W_0 + \gamma U$
on isochores.

Last ingredient in equation of state:
$U = U_0 + \alpha T^{3/5}$
on isochores.
[Rosenfeld & Tarazona, Mol. Phys., (1998)]
(Does not hold for Wahnstrom BLJ)
[Pedersen, PRL (2010)]

IPL: $W = \gamma U$

[Schrøder et al., arXiv:1004.5145 (2010), paper V]

Conclusion

Two state points: $(\rho_1,\ T_1)$ and $(\rho_2,\ T_2)$

Considering pairs of micro-states related by:

$$\rho_1^{1/3}\mathbf{r}_i^{(1)} = \rho_2^{1/3}\mathbf{r}_i^{(2)} \qquad (i = 1, \ldots N)$$

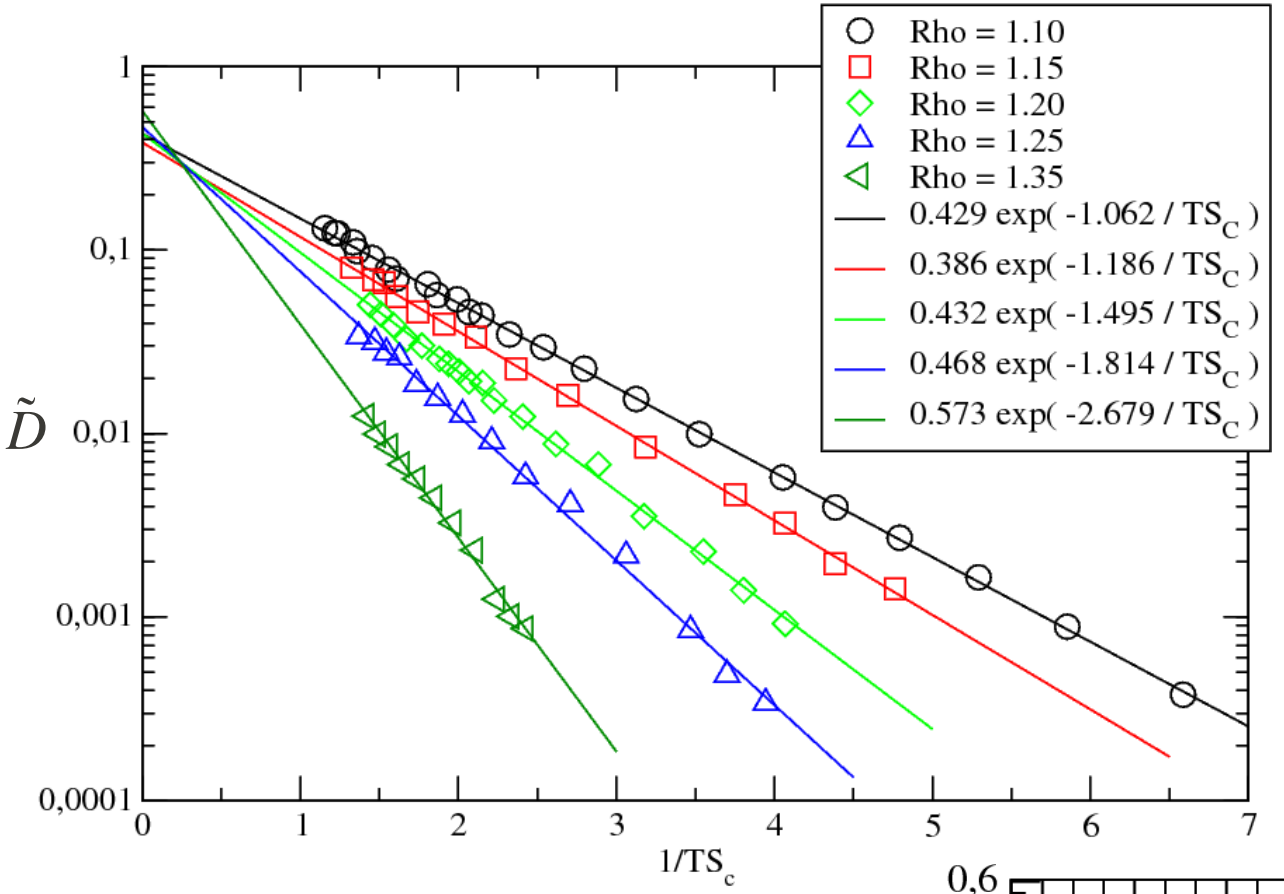
State points are isomorphic if all "physically relavant" pairs of micro-states fullfill:

$$e^{-U(\mathbf{r}_1^{(1)},\ldots,\mathbf{r}_N^{(1)})/k_BT_1} = C_{12}e^{-U(\mathbf{r}_1^{(2)},\ldots,\mathbf{r}_N^{(2)})/k_BT_2}$$

From this assumption follows a number of properties:

- Invariant on an isomorphic curves in state diagram:
  - Excess entropy, $S_{ex} = S - S_{ideal}$.
  - Structure (in reduced units, $\tilde{\mathbf{r}}_i \equiv \rho^{1/3}\mathbf{r}_i$).
  - Dynamics (in reduced units, $\tilde{t} = t\rho^{1/3}\sqrt{kT/m}$), including high-order correlation functions.

  → Shape of isomorphs in generalized LJ systems
- W(t) and U(t) are strongly correlated.
- Isochores are straight lines in W,U-plot. → Equation of state
- Jumps between isomorphic state points are instantenous!
- The isomorphic filter, e.g: $D \neq D_0 \exp(-A/TS_c)$



Making Adam-Gibbs pass the isomorpic filter:

$$\tilde{D} = D_0 \exp\left(-A(\rho)/TS_c\right)$$

$$\tilde{D} \equiv D\,\rho^{1/3}(kT/m)^{-1/2}$$

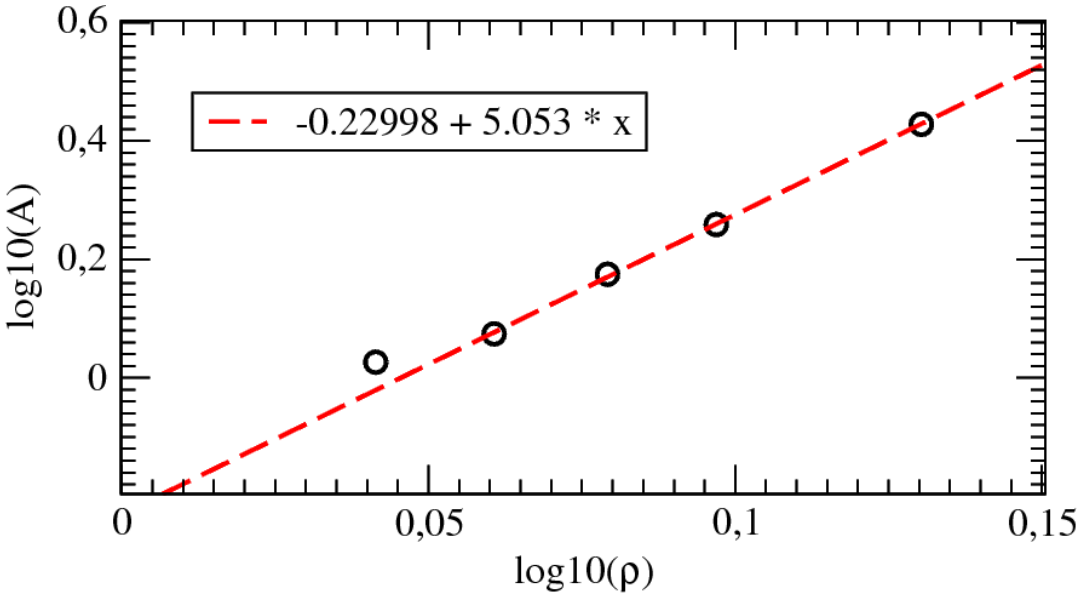
Data from:
[Sastry, PRL (2000)]

Expectation:
$$A(\rho) \sim \rho^{\gamma}$$

Very recent collaboration:
[Sastry & Schrøder, KITP (2010)]

Vi find: $\gamma = 5.05$

Thermodynamics gave ($\rho = 1.2$):
$\gamma = 5.16$



Thank you for your attention!