

Strong pressure-energy correlations in liquids

Origin and Consequences

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Outline

1 Strong W-U correlations

The Lennard-Jones liquid

A class of SC-Liquids

2 Origin

Soft-sphere r^{-n} liquids

Effective inverse power-law

Approximate $ar^{-n} + br + c$ pair-potential.

Super-critical Argon (experimental)

3 Viscous liquids

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Density scaling

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6 Summary

Strong W-U Correlations in the Lennard-Jones liquid

Molecular dynamics simulations: Solving classical equations of motion

$\frac{\partial^2 \mathbf{x}_i}{\partial t^2} = \frac{F_{x,i}}{m_i}$ by numerical integration. **Constant V and T.**

The well-studied Lennard-Jones liquid:

$$U_{\text{pair}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

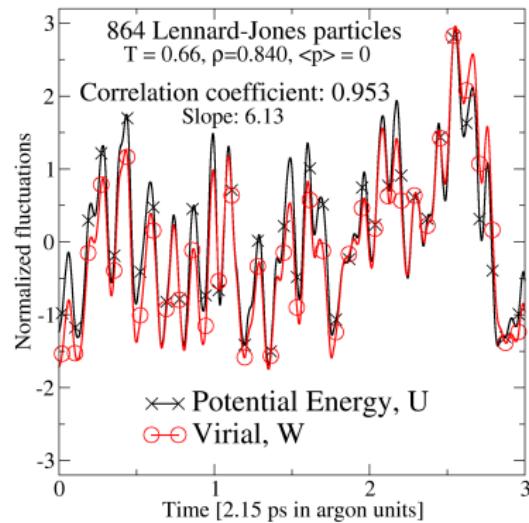
$$E = K + U$$

$$pV = Nk_B T + W$$

W/V (Virial per volume):

Configurational part of pressure.

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



Two important numbers:

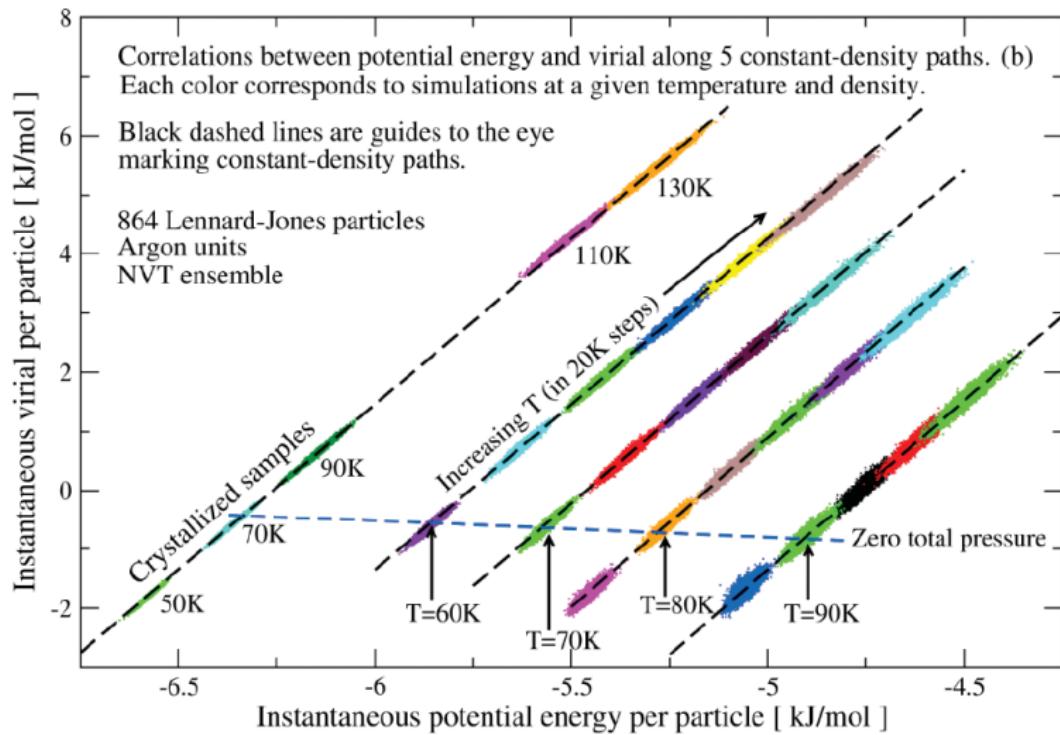
$$R \equiv \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}} = 0.953 \quad \&$$

$$\gamma \equiv \sqrt{\frac{\langle (\Delta W)^2 \rangle}{\langle (\Delta U)^2 \rangle}} = 6.13$$

Questions

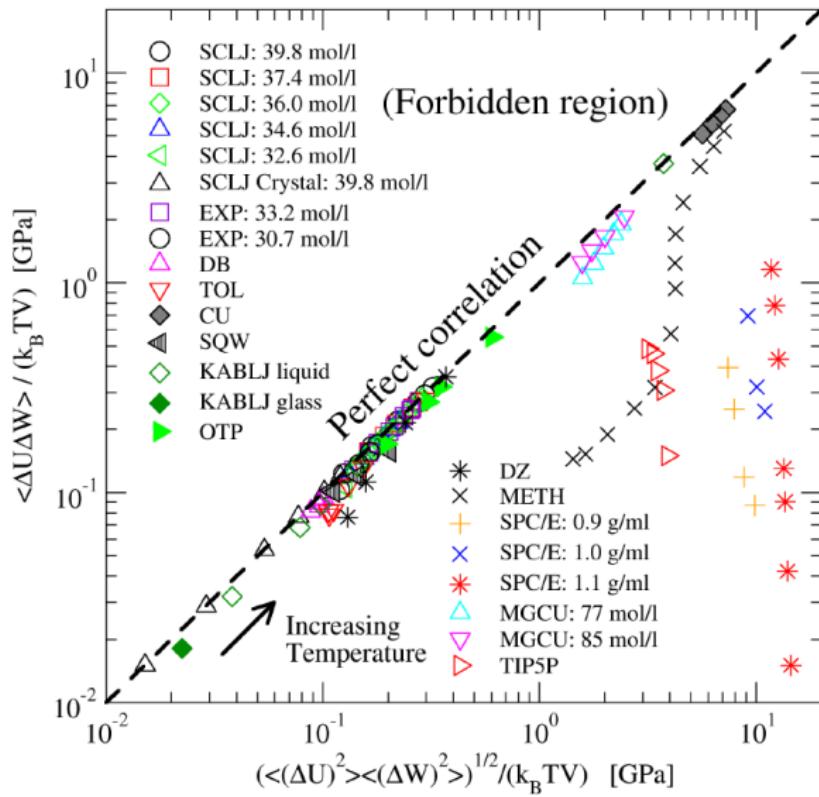
- Phenomenology: How general is this?
- Analysis: What causes such strong correlations?
- Consequences: Is this important?

More state points



Slope: $\gamma \equiv \sqrt{\frac{\langle (\Delta W)^2 \rangle}{\langle (\Delta U)^2 \rangle}} \approx 6$. Survives first-order phase transition!

Strongly correlating liquids (SCL)



NVT ensemble:

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

$$-1 < R < 1$$

SCL:

van der Waals, metals

non-SCL:

Hydrogen-bonded, Ionic, Covalent

Origin: Recall soft-sphere r^{-n} liquids

Pair interaction of inverse power-law,

$$U_{\text{pair}} = \varepsilon \left(\frac{r}{\sigma} \right)^{-n}.$$

Pair virial,

$$W_{\text{pair}} = -\frac{1}{3} r \frac{\partial U_{\text{pair}}}{\partial r} = \frac{n\varepsilon}{3} \left(\frac{r}{\sigma} \right)^{-n}.$$

Thus ($U = \sum_{\text{pairs}} U_{\text{pair}}$ and $W = \sum_{\text{pairs}} W_{\text{pair}}$),

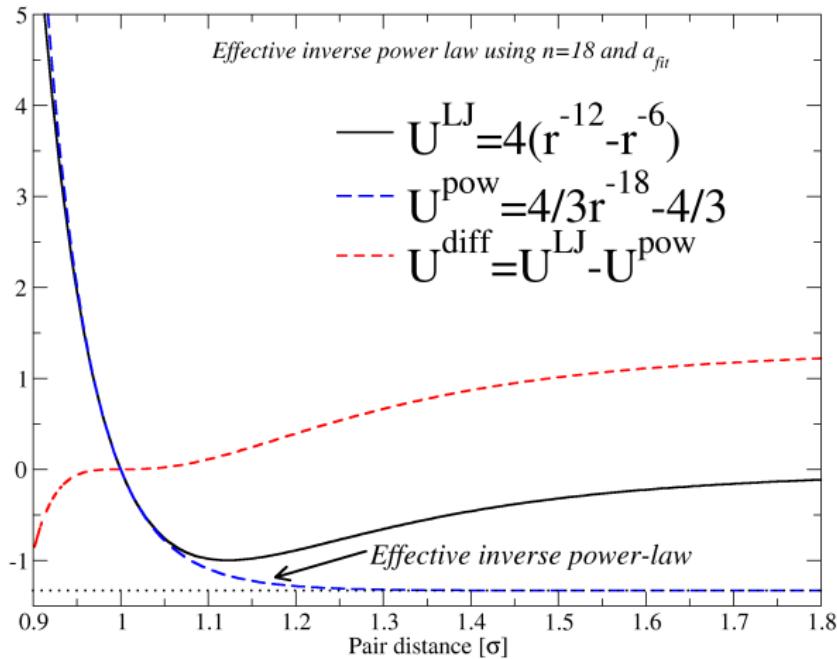
$$U = \gamma W$$

where

$$\gamma = n/3.$$

Correlation is exact $R = 1$ and trivial.

Fitted inverse power-law (IPL)

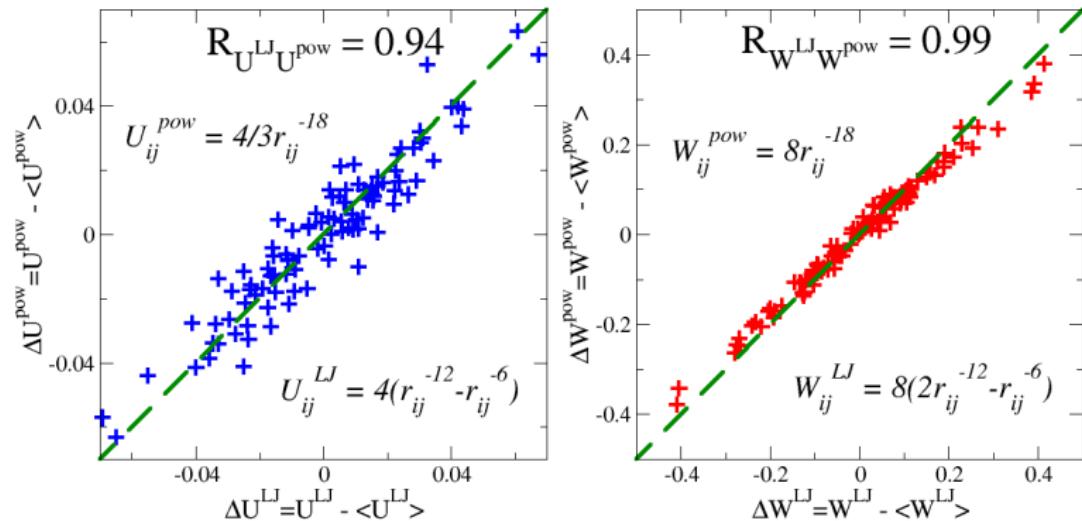


$n = 18 \Rightarrow \gamma = n/3 = 6$. Close to the right exponent.

Lennard-Jones vs. r^{-n} energy

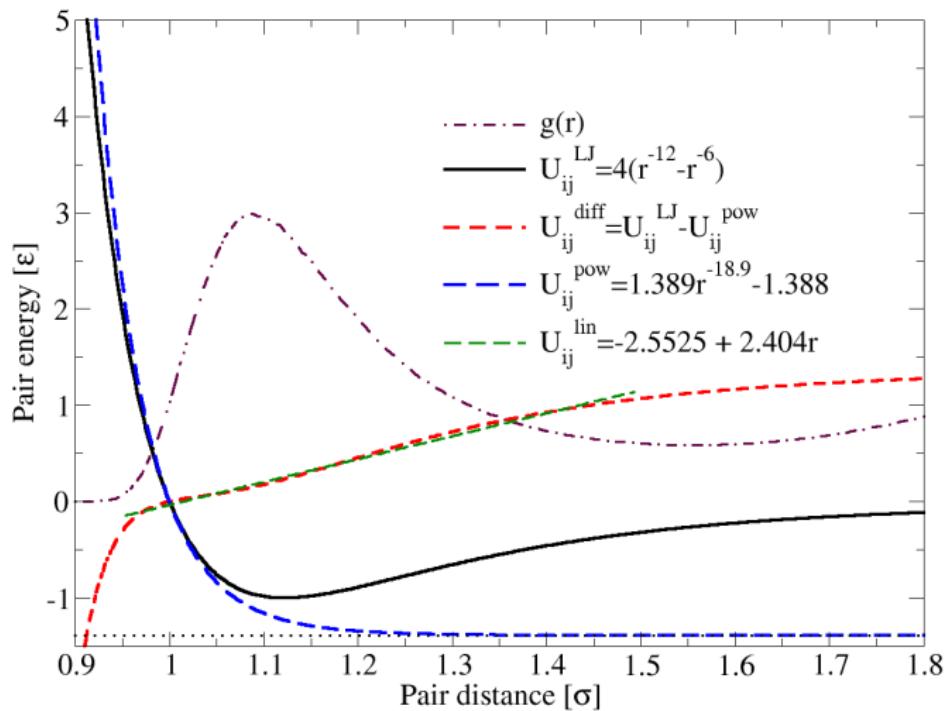
864 Lennard-Jones particles

$T = 0.66, \rho = 0.840, \langle p \rangle = 0$



Calculated for the same configurations.
 Inverse power-law accounts for fluctuations
 (even at zero pressure)

The best IPL ar^{-n} to describe fluctuations



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

Why $\sum(br + c)$ almost doesn't fluctuate at constant volume

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



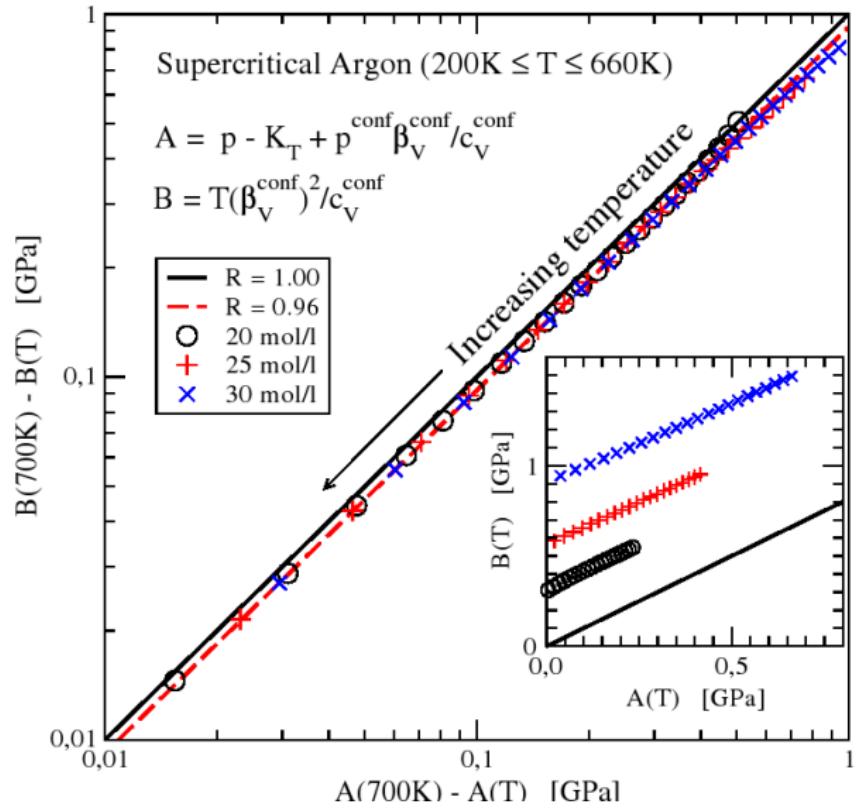
$$\sum_{i>j} r_{ij} = L$$



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

Qualitatively same explanation of dense liquid/crystal in three dimensions:
see Ref. [Bailey et al., JCP 129:184508 (2008)].

Super-critical Argon (experimental data from NIST)



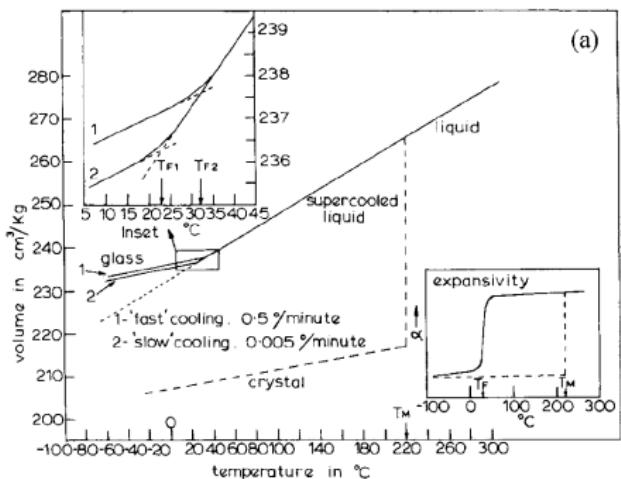
$$\text{FD relation: } c_V^{\text{conf}} = c_V - \frac{3}{2} N k_B = \frac{\langle (\Delta U)^2 \rangle_{VT}}{k_B T^2}.$$

R from (static) response functions: c_V , β_V and K_T (and approximations, [PRL 100, 015701 (2008)])

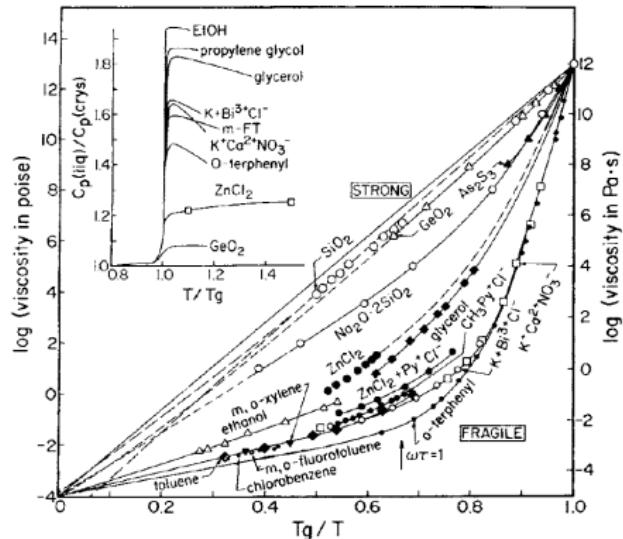
$$R \approx 0.96$$

Inset: IPL equation of state does not work.

Super cooled liquids



Volume of Se. From Ref. [Owen, 1985]
(data: [Dzhalilo and Rzaev, 1967])



From Ref. [Angell, 1985]

Review: [Debenedetti & Stillinger, Nature 410:259 (2001)]

Frequency-dependent response functions

Fluctuation-dissipation theorem

Imaginary part of frequency-dependent response functions (NVT):

Isochoric specific heat capacity per unit volume, $c_V = T \left(\frac{\partial S}{\partial T} \right)_V$

$$c_V''(\omega) = \frac{\omega}{V k_B T^2} C_\omega \{ \langle \Delta E(0) \Delta E(t) \rangle_{VT} \}$$

Isothermal bulk modulus, $K_T = V \left(\frac{\partial p}{\partial V} \right)_T$

$$K_T''(\omega) = -\frac{\omega V}{k_B T} C_\omega \{ \langle \Delta p(0) \Delta p(t) \rangle_{VT} \}$$

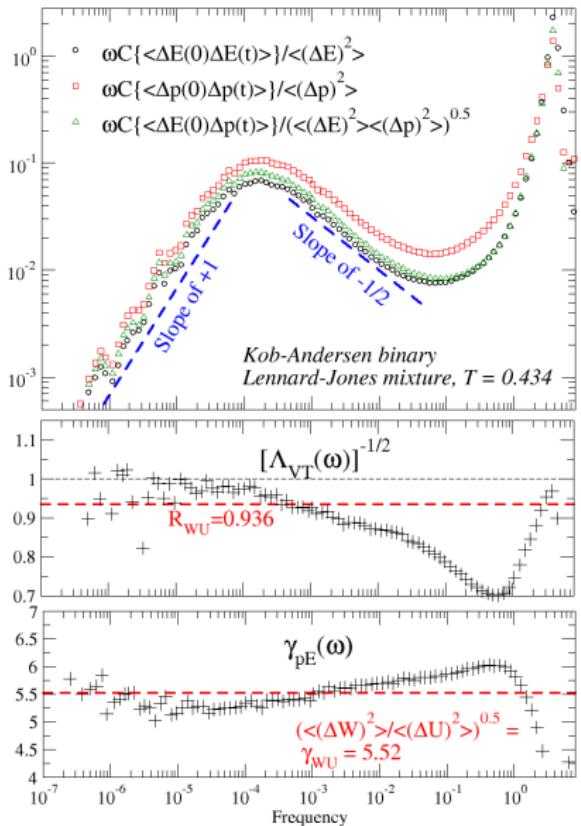
Isochoric pressure coefficient, $\beta_V = \left(\frac{\partial p}{\partial T} \right)_V$

$$\beta_V''(\omega) = \frac{\omega}{k_B T^2} C_\omega \{ \langle \Delta E(0) \Delta p(t) \rangle_{VT} \}.$$

$\Delta E(slow) = \Delta U(slow)$ and $V \Delta p(slow) = \Delta W(slow)$, thus for SCL:

$$c_V''(\omega) \propto K_T''(\omega) \propto \beta_V''(\omega)$$

Dynamic Prigogine-Defay ratio



Dynamic Prigogine-Defay ratio
[Ellegaard et al., JCP 126, 074502 (2007)]:

$$\Lambda_{VT}(\omega) \equiv -\frac{c_V''(\omega) K_T''(\omega)}{T [\beta_V''(\omega)]^2}$$

$$= \frac{C_\omega \{ \langle \Delta E(0) \Delta E(t) \rangle_{VT} \} C_\omega \{ \langle \Delta p(0) \Delta p(t) \rangle_{VT} \}}{[C_\omega \{ \langle \Delta E(0) \Delta p(t) \rangle_{VT} \}]^2}$$

$$[\Lambda_{VT}(\omega)]^{-1/2} \simeq R_{WU}$$

$$\gamma_{pE}(\omega) = \sqrt{\frac{-K_T''(\omega)}{T c_V''(\omega)}} \simeq \gamma_{WU}$$

[Pedersen et al., PRE 77, 011201
(2008)]

Rethinking the (classical) Prigogine-Defay ratio

Davies & Jones [1953]

$$\Pi_{pT} = \frac{\Delta c_p \Delta \kappa_T}{T_g (\Delta \alpha_p)^2}$$

where $\Delta \rightarrow$ change at glass-transition. If "single parameter" at glass transition then $\Pi_{pT} = 1$.

However, $2 < \Pi_{pT} < 4$ [Moynihan et al., 1976]. Concept abandoned (not well-defined; "glass transition" is not genuine phase transition).

Strongly correlating glass formers

Liquid and corresponding glass (fast experiments on eq. liquid).

$$\Pi_{VT} \equiv -\frac{\Delta c_V \Delta K_T}{T_g (\Delta \beta_V)^2} \simeq (R_{WU})^{-2} \simeq 1 \text{ and } \gamma_{WU} \simeq \sqrt{\frac{-\Delta K_T}{T \Delta c_v}}$$

If $\Pi_{VT} = 1$ then $\Pi_{pT} = 1$.

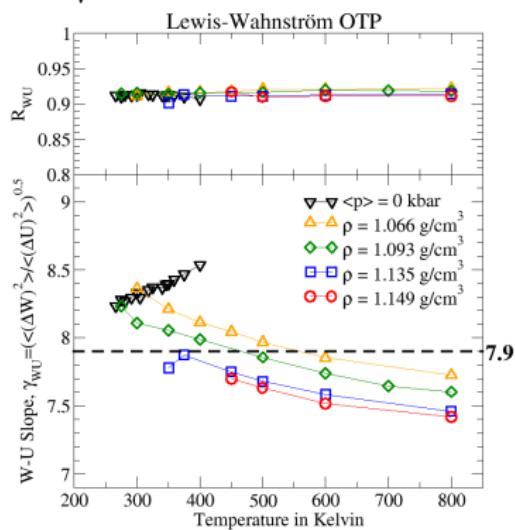
Literature values of the Prigogine-Defay ratio

Material	Π_{pT}	$\Pi_{pT}^{-1/2}$	
Pure SiO ₂ glass	$10^3\text{-}2\cdot10^5$	0.03-0.002	
Glycerol, C ₃ H ₅ (OH) ₃	9.4	0.33	
GeO ₂	6.9 ± 1.3	0.38 ± 0.04	
16Na ₂ O10B ₂ O ₃ 74SiO ₂	4.9	0.45	
B ₂ O ₃	4.7	0.46	
0.4Ca·NO ₃ ·0.6KNO ₃	4.5	0.47	
Glucose, OC ₆ H ₇ (OH) ₆	3.7	0.52	
16Na ₂ O10CaO74SiO ₂	3.6	0.53	
Se	2.4	0.65	
ZrTiCuNiBe	2.4	0.65	
26Na ₂ O74SiO ₂	2.3	0.66	
Polyvinylacetate	2.2(1.7)	0.67(0.77)	$\Pi_{pT} \simeq 1$ for van der Waals bonded glass formers.
n-Propanol, C ₃ H ₇ OH	1.9	0.73	
Polyvinylchlorid, PVC	1.7	0.77	
Polystyrene, PS	1.3 ± 0.1 (16)	0.88 ± 0.03 (0.25)	
OTP(75%)-TPCM(25%)	1.28	0.88	
OTP(67%)-OPP(33%)	1.20 ± 0.05	0.92 ± 0.02	
Polystyrene, PS	1.085	0.96	
Phenoxy	1.03	0.99	
Polycarbonate	1.02	0.99	
Polysulfone	0.96	1.02	
Polyarylate	0.90	1.05	
Polyisobutene	0.9	1.05	

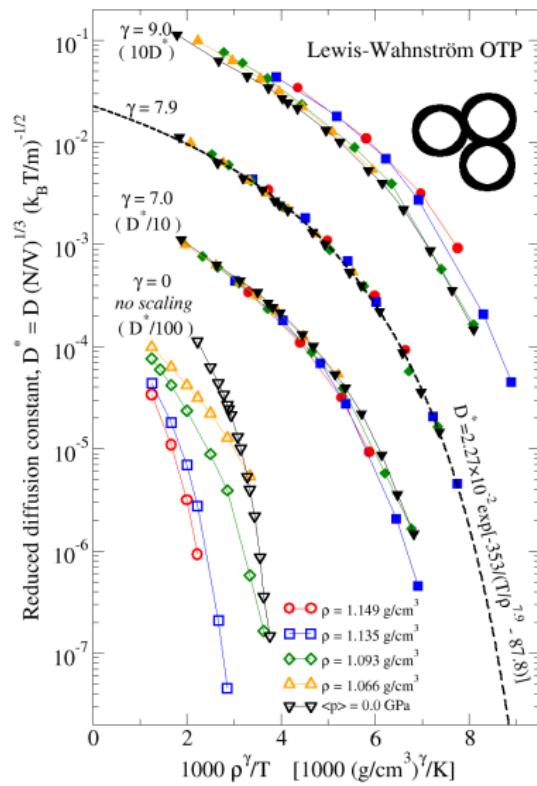
Density scaling: A model liquid

SCL inherits the scale invariance of r^{-n} -liquids:

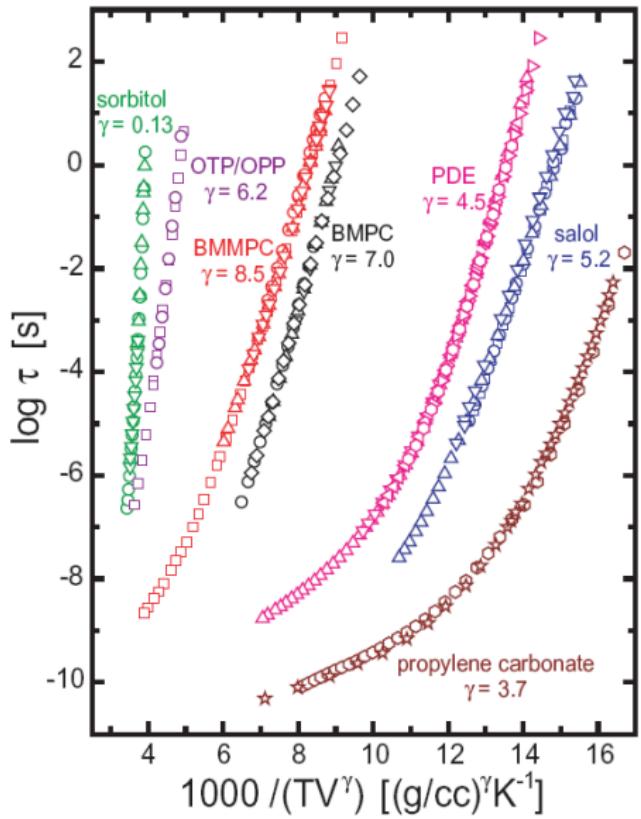
$\Gamma = \rho^\gamma / T$ with $\gamma = \sqrt{\frac{\langle (\Delta W)^2 \rangle}{\langle (\Delta U)^2 \rangle}}$ are the same in
 $v_s \equiv \sqrt{\frac{k_B T}{m}}$ and $I_s \equiv \left(\frac{N}{V}\right)^{-1/3}$ units.



LW-OTP: ortho-terphenyl model



Density scaling: Experiments



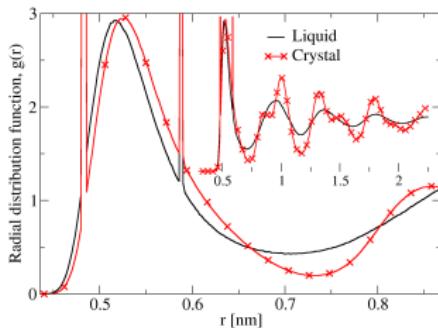
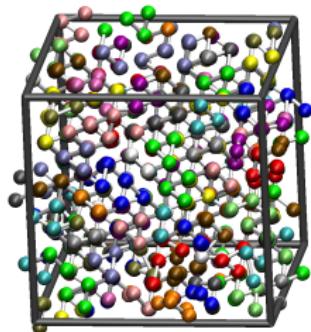
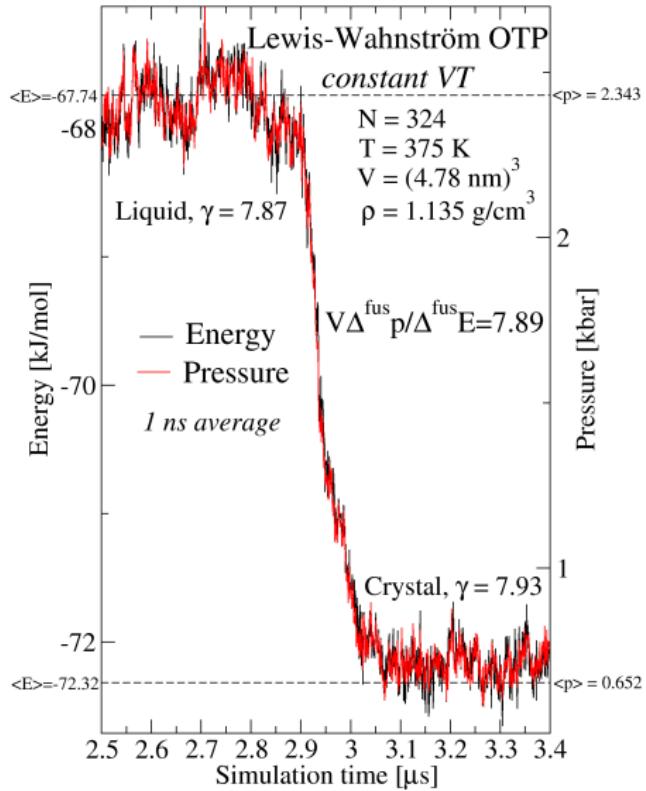
$$\tau = f(\rho^\gamma / T)$$

From [Roland et al., Rep. Prog. Phys. 68, 1405 (2005)]

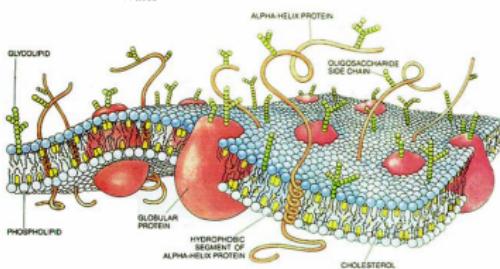
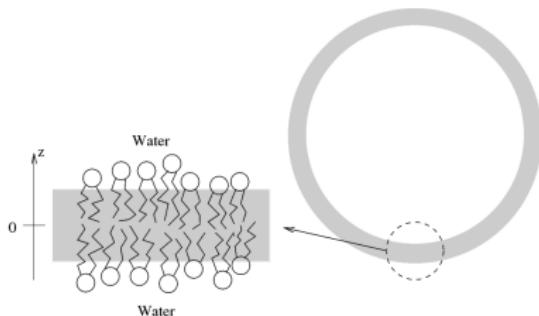
Reanalyzing OTP-OPP glass transition data from
[Takanhara et al., 1999]:

$$\sqrt{\frac{-\Delta K_T}{T \Delta c_v}} = 6.0 \simeq \gamma_{\text{scaling}}$$

Crystallization of a strongly correlating liquid



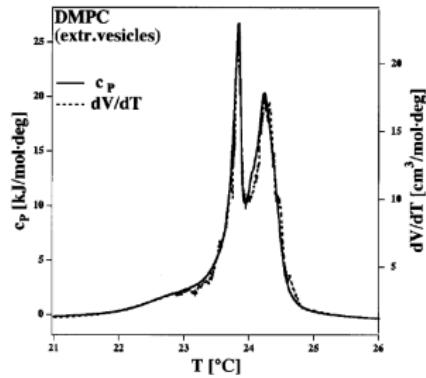
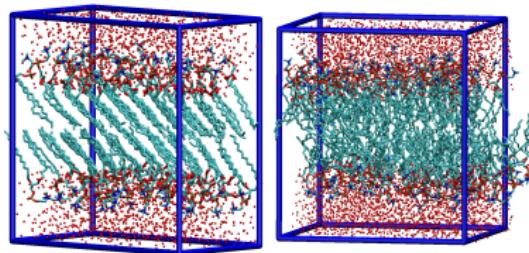
Phospholipid- and biological membranes



[Scientific American 253:86 (1985)]

Motivation: Soliton sound waves:

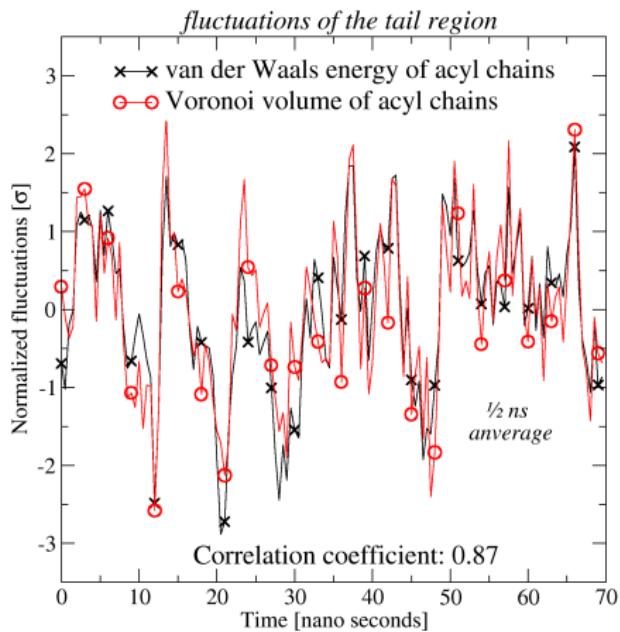
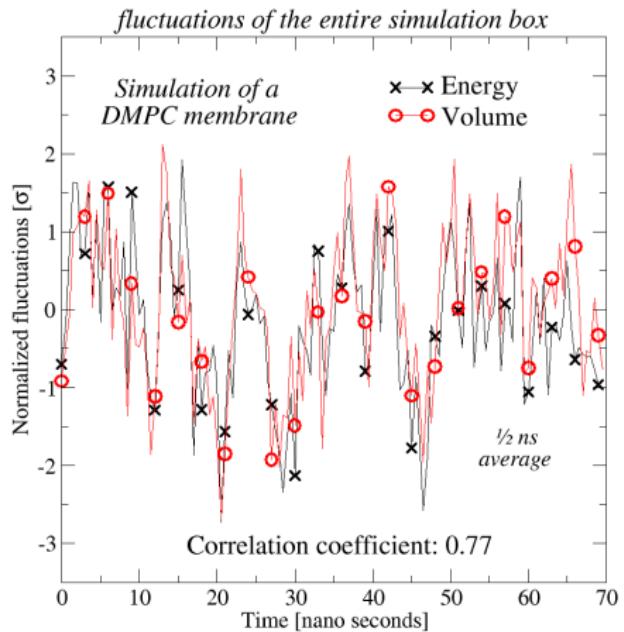
[Heimburg & Jackson (2005) PNAS 102:9790]



[Ebel et al. (2001) JCP-B 105:7353]

$$H_i \propto V_i \Rightarrow \alpha_p(T) \propto c_p(T)$$

Phospholipid membranes



in collaboration with Günther Peters (Technical University of Denmark)

Summary

- Strongly correlating liquids are simpler than liquids in general.
- These liquids' fluctuations are approximately described by radially symmetric extended inverse power-law $ar^{-n} + br + c$ (IPL equation of state do not work, though).
- Strongly correlating liquids include van der Waals liquids and metals, but not hydrogen-bonding, covalently bonded, or ionically bonded liquids.
- Slow fluctuation of phospholipid membranes are strongly correlating

References:

- Brief:** U. R. Pedersen et al., PRL 100, 015701 (2008)
- Comprehensive:** N. P. Bailey et al., JCP 129, 184507 & 184508 (2008)
- Viscous liq. response:** U. R. Pedersen et al., PRE 77, 011201 (2008)
- Scale-invariance:** T. B. Schrøder et al., arXiv.org:0803.2199
- Off-equilibrium dyn.** T. B. Schrøder et al., arXiv.org:0903.0516
- Biomembranes:** U. R. Pedersen et al., arXiv.org:0811.3317
- urp phd-thesis:** Available at the web, urp.dk