# Do all liquids become strongly correlated at high pressure?

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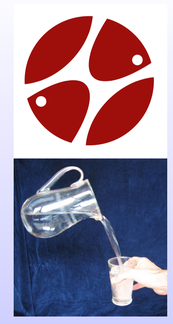


## Motivation

**Recent results [1] show that**

- Simple liquids show strong correlations (e.g. Lennart-Jones)
- Multiple interaction liquids like methanol (van der Waals and Hydrogen bonding) show weak correlations
- Methanol becomes strongly correlating as temperature is taken to extreme along an isochor

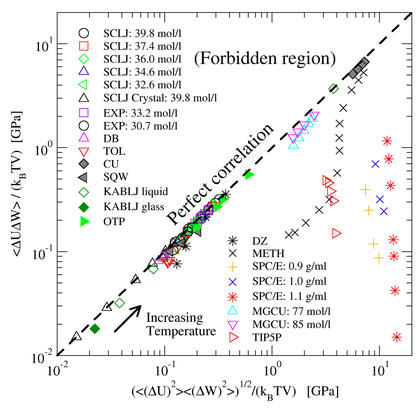



*figure taken with permission from reference [1]*

**The results suggests that**

- Correlation increases with increasing density along isotherms

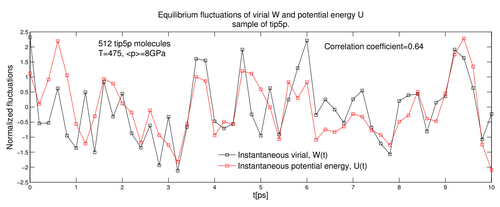
## Systems studied

- Single-component Lennart-Jones. N=864 particles; same parameters used as in reference [2]
- 3-site model of methanol [3]. N=1728 particles
- United-atom model [4] ionic liquid 1-Butyl-3-methylimidazolium Nitrate, $[BMIM]^+[NO_3]^-$. N=210 of each ion.
- TIP5P water model [5]. N=512

## Simulation details

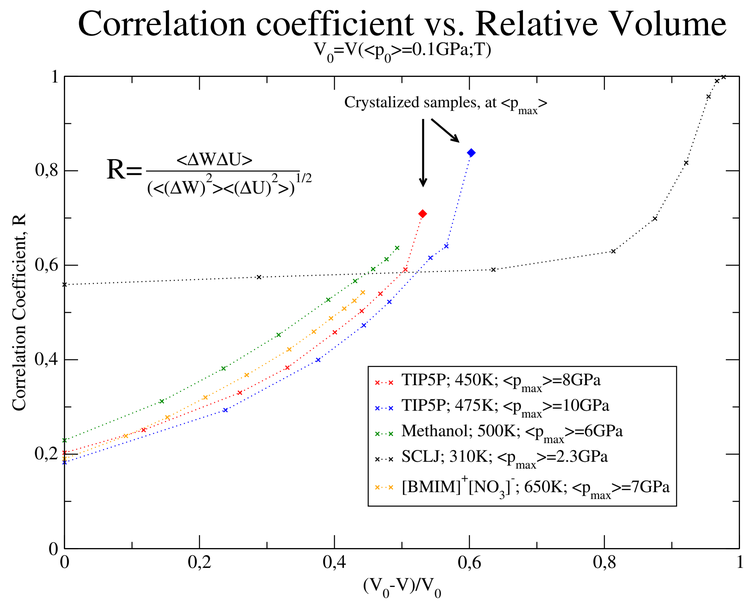
- Pressure was changed along isotherms by varying the density
- Systems were equilibrated in the NVT-ensemble
- Data was collected from 10 ns long production runs in the NVT-ensemble

## Snap-shot of studied quantities




*Normalized equilibrium fluctuations in potential energy and virial.*

## Results




Calculated cross-correlation between instantaneous equilibrium fluctuations in Virial, W, and potential energy, U, as a function of relative volume. Averages are calculated over full length of simulations (10 ns) after equilibration.

## First comment on results

**The results imply**

- Single-component Lennart-Jones liquid is not always strongly correlating as suggested by figure in the *Motivation* box
- Density wins over temperature

## Second comment on results

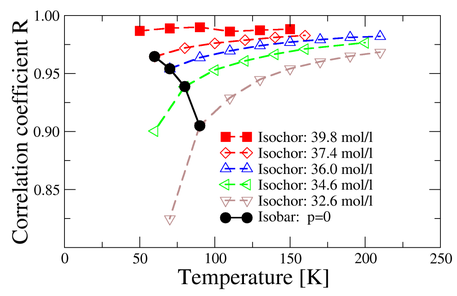



*figure taken with permission from reference [1]*

- The figure explains the weak correlation of the single-component Lennart-Jones liquid.
- Can be seen by extrapolating the 0-isobar to high temperature state-points

## Conclusion

**The simulations imply**

$$\left(\frac{\partial R}{\partial \rho}\right)_T > 0$$

- Not all liquids become strongly correlating - they crystalize on their way

## References

[1] N.P. Bailey, U.R. Pedersen, N. Gnan, T.B. Schrøder, and J.C. Dyre (2008), to appear in *J. Chem. Phys*; *arXiv:0807.0550v2 [cond-mat.soft]*.
[2] U.R. Pedersen, N.P. Bailey, T.B. Schrøder, and J.C. Dyre, *Phys. Rev. Lett*, **100**, 015701 (2008).
[3] W.F. Van Gunsteren, et.al. *Biomolecular Simulation: The GROMOS96 manual and user guide*, (1996).
[4] N.M. Micaelo, A.M. Babtista, and C.M. Soares, *J. Phys. Chem. B*, **110**, 14444-14451 (2006)
[5] M.W. Mahoney and W.L. Jorgensen, *J. Chem. Phys*. **112**, 8910 (2000).