2007 NCNR Summer School on Methods and Applications of Neutron Spectroscopy

ROOM

Density Fluctuations in Liquids

– from rubidium to water, and to complex metallic liquids

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Unlike solids and gases, liquids do not allow a general calculation of their thermodynamic quantities or even their temperature dependence. The reason for this is the presence of strong interactions between the molecules of the liquid without having at the same time the smallness of the vibrations which makes the thermal motion of solids so simple. The intensity of the molecular interaction makes it impossible to know when calculating thermodynamic quantities, the actual law of interaction, which varies for different liquids. The only thing which can be done in general form is the study of the properties of liquids near absolute zero.

– L. D. Landau and E. M. Lifshitz,
Course of Theoretical Physics 5: Statistical Physics
translated by E. Peierls and R. F. Peierls (Pergamon Press, 1958)
Chapter VI, 66, pp. 198-199.

- Rubidium:

  thermal fluctuations

- Water:

  thermal + phase fluctuations

- Glass-Forming Metallic Liquids:

  thermal + phase + concentration fluctuations

Phonons in Liquids

VOLUME 32, NUMBER 2 PHYSICAL REVIEW LETTERS 14 JANUARY 1974

Short-Wavelength Collective Excitations in Liquid Rubidium Observed by Coherent Neutron Scattering*

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(Received 12 November 1973)

PHYSICAL REVIEW A VOLUME 9, NUMBER 4 APRIL 1974

Density fluctuations in liquid rubidium. I. Neutron-scattering measurements*

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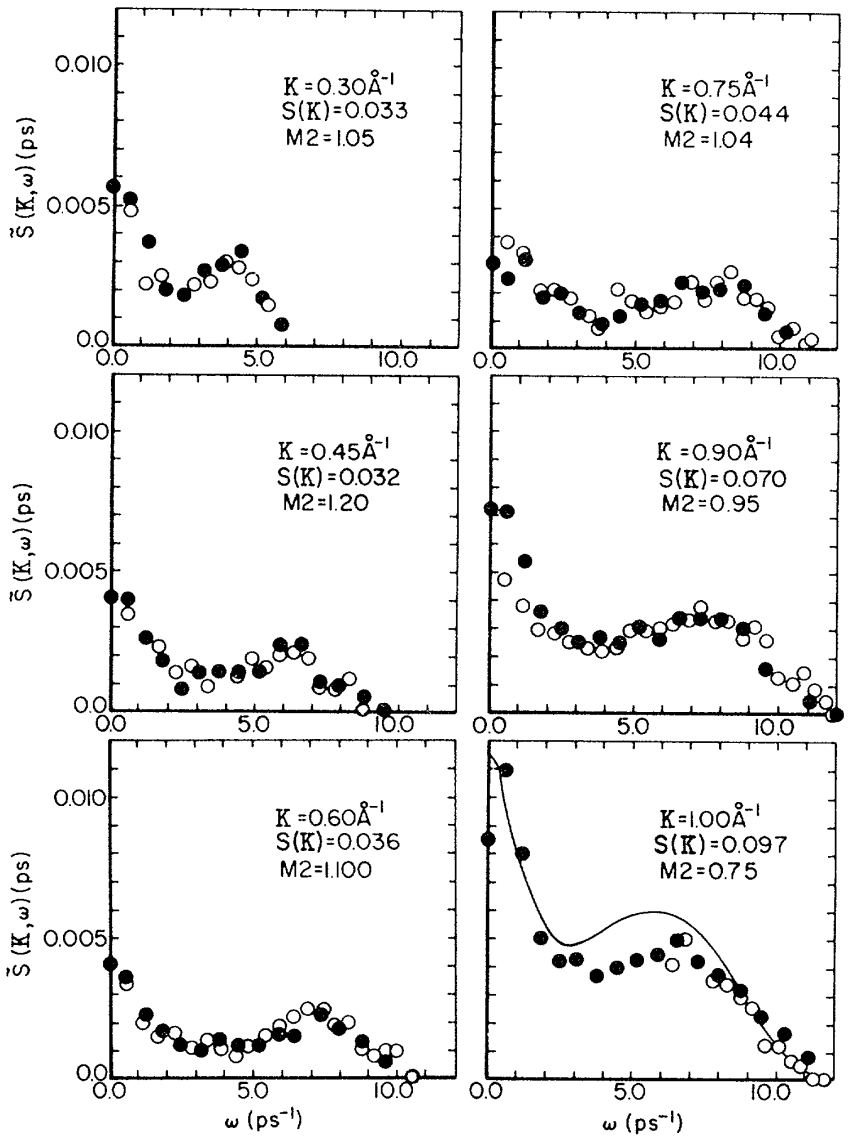
(Received 15 November 1973)

- *vs.* Solid rubidium
- Multiple-scattering correction
- Small Q, Kinetic Constraint
- Rahman & Price

Evidence of Long Wavelength Longitudinal Acoustic Mode



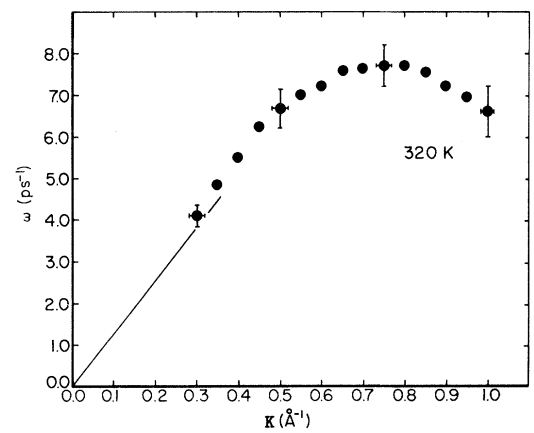


FIG. 2. "Dispersion curve" for liquid rubidium derived from the measured $\tilde{S}(\kappa,\omega)$. Error estimates reflect the width of the observed peaks and the resolution in κ. Solid line, derived from the measured sound velocity (Ref. 16).

FIG. 1. Representative results for the symmetrized scattering $\tilde{S}(\kappa,\omega)$ of liquid rubidium at constant values of κ. Open (closed) circles represent neutron energy loss (gain). The statistical errors are smaller than the points; estimates of systematic errors are given by the scatter of the points. Note the large scatter near $\omega = 0$ which arises from a correction described in the text. Solid line for $\kappa = 1.0$ Å^{-1}, results obtained from another experiment (Ref. 8). Also shown, the zeroth moment $S(\kappa)$ and the ratio of the measured to the exact second moment $M2$ for each κ.

No Long Wavelength Longitudinal Acoustic Mode

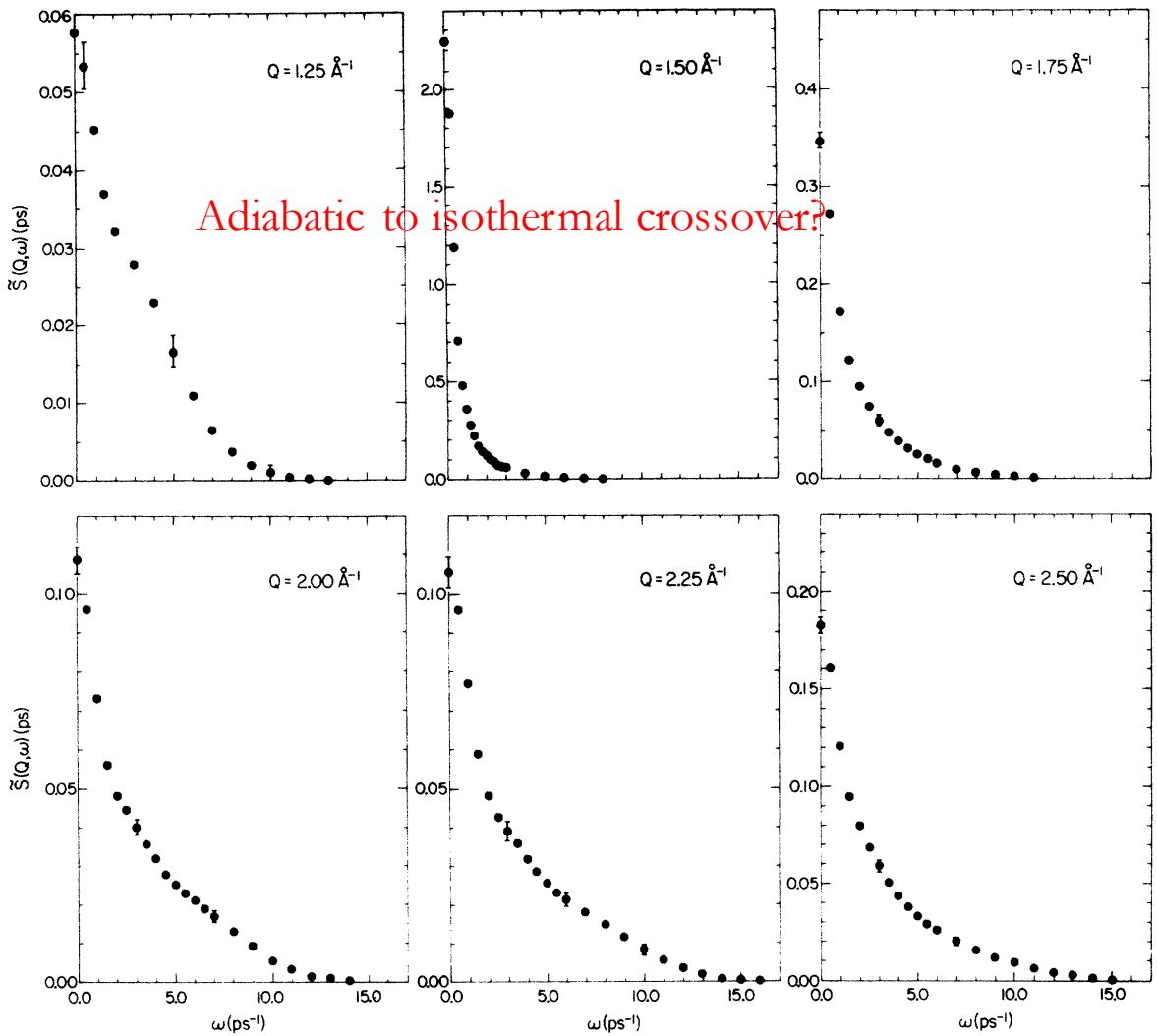


FIG. 5. Scattering function $\tilde{S}(Q,\omega)$ for six values of Q between 1.25 and 2.5 Å^{-1}. These results were obtained from experiment 1.

No Long Wavelength Longitudinal Acoustic Mode

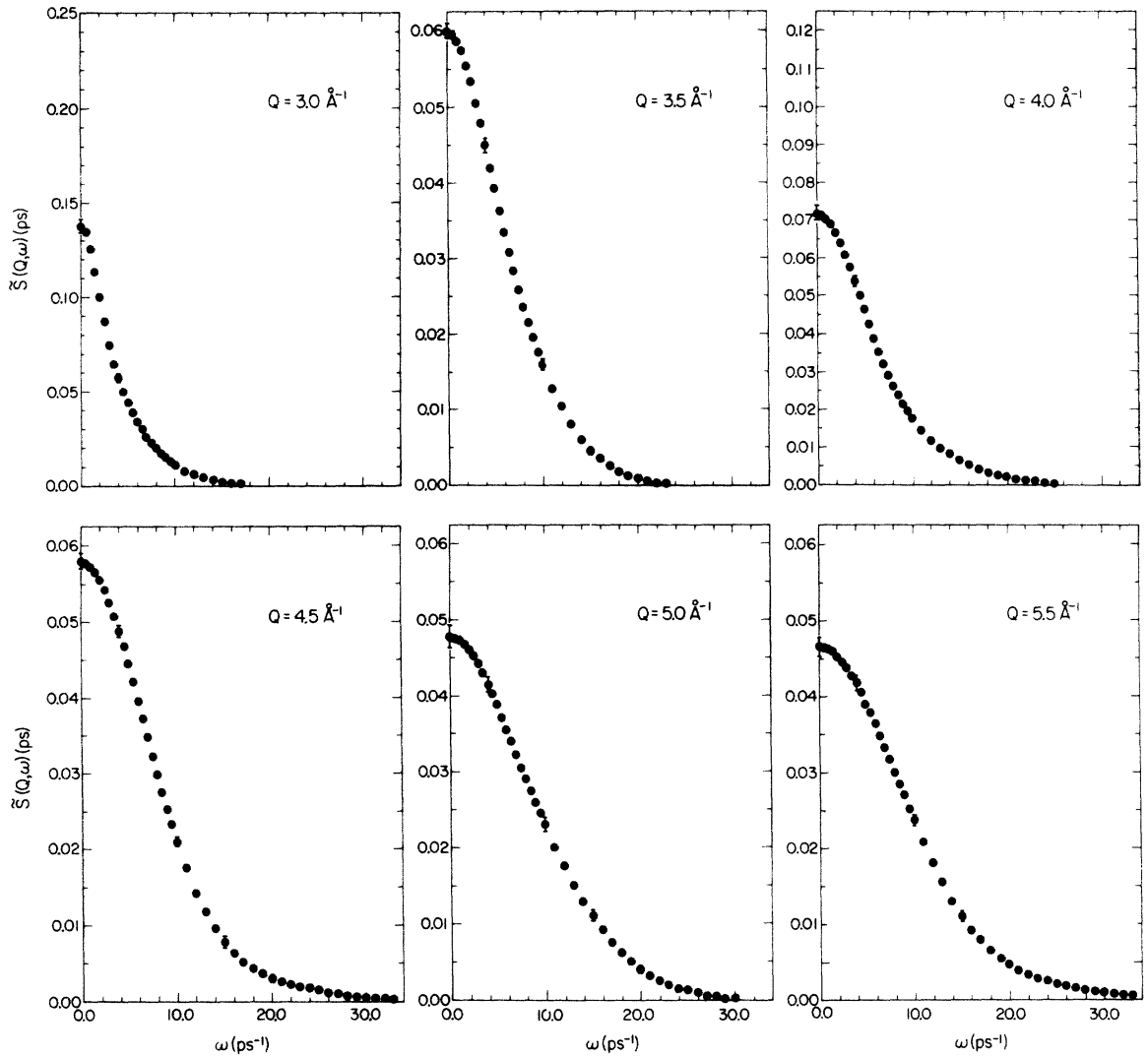


FIG. 6. Scattering function $\tilde{S}(Q,\omega)$ for six values of $Q \geq 3.0$ Å^{-1}. These results were obtained from experiment 2.

The dynamic properties of monatomic liquids

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Abstract

The computer simulation and inelastic neutron scattering studies of simple, monatomic liquids are reviewed, together with the theory appropriate for their interpretation. All three aspects of the dynamic properties of monatomic liquids began a new era of development around 1965, and the review is concerned chiefly with the experiments and theory reported in the intervening decade.

Computer simulation (molecular dynamics) studies have featured strongly in the development of non-equilibrium statistical mechanics techniques for the calculation of correlation functions that enter the various measured susceptibilities. In fact molecular dynamics studies of systems interacting via continuous potentials have developed to the level of sophistication where they set a standard for neutron scattering experiments. The neutron experiments are difficult to perform with high accuracy, yet they offer a unique means of investigating the dynamics of simple liquids in the domain of wavevectors and frequencies larger than about 0·05 Å^{-1} and $5 \times 10^{11}\ \text{s}^{-1}$ respectively. The problems faced in analysing neutron data to the level required today are reviewed in detail, with particular attention to multiple scattering corrections. A review of neutron experiments on monatomic liquids shows that surprisingly few bear close scrutiny today. Theory has developed through the rigorous generalization of the Markovian theory of fluctuations set out by Landau and Lifshitz (1959). The development has taken the form of a generalized Langevin equation, proposed by Zwanzig (1961) and Mori (1965a), which provides a framework within which neutron and molecular dynamics data may be interpreted. The technique is reviewed, related to linear response theory, and used to summarize the recent theories.

This review was completed in October 1974.

Rep. Prog. Phys. 1975 **38** 461–563

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- Liquid Rubidium:

  thermal fluctuations

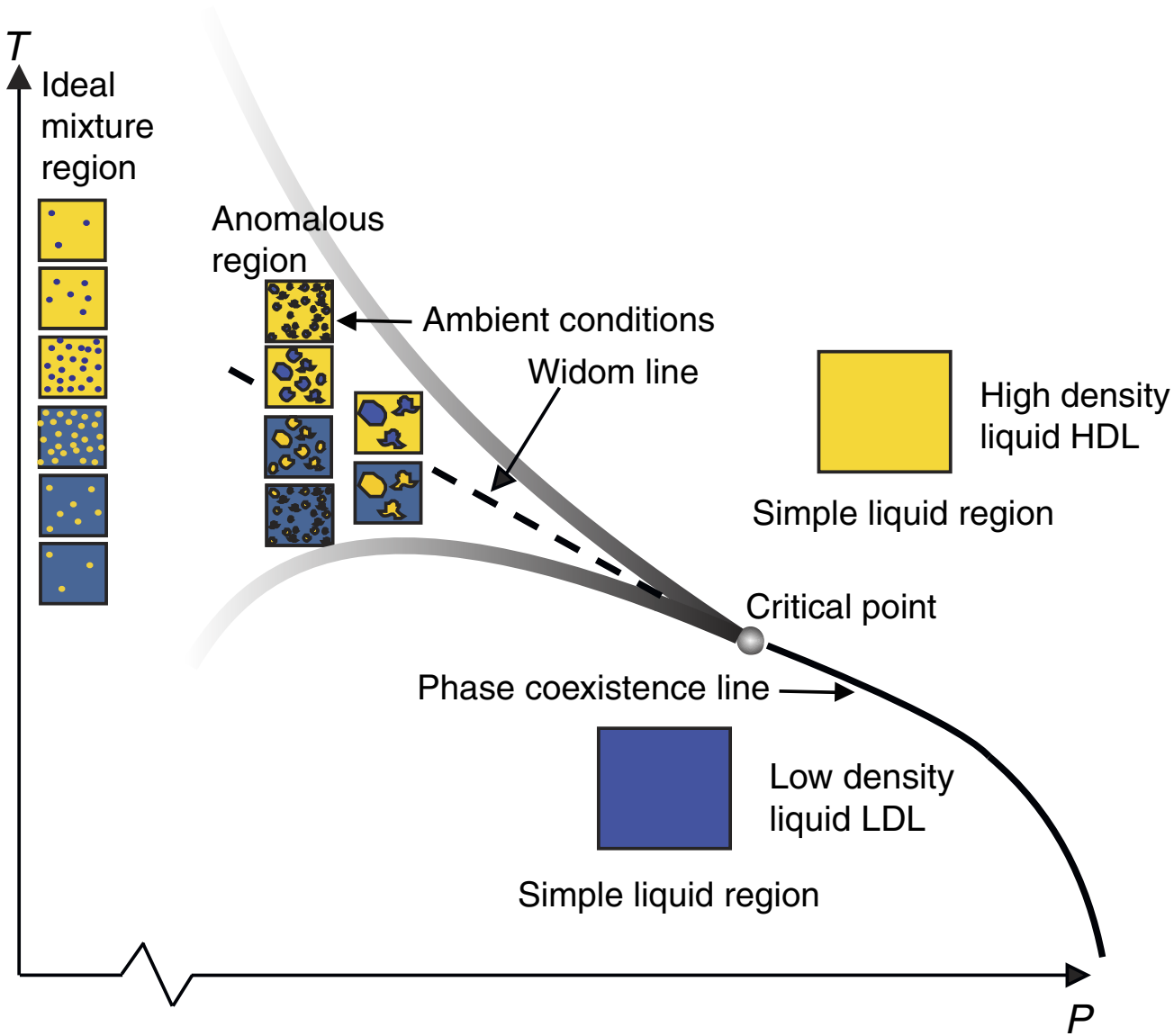
- Water:

  thermal + phase fluctuations

- Glass-Forming Metallic Liquids:

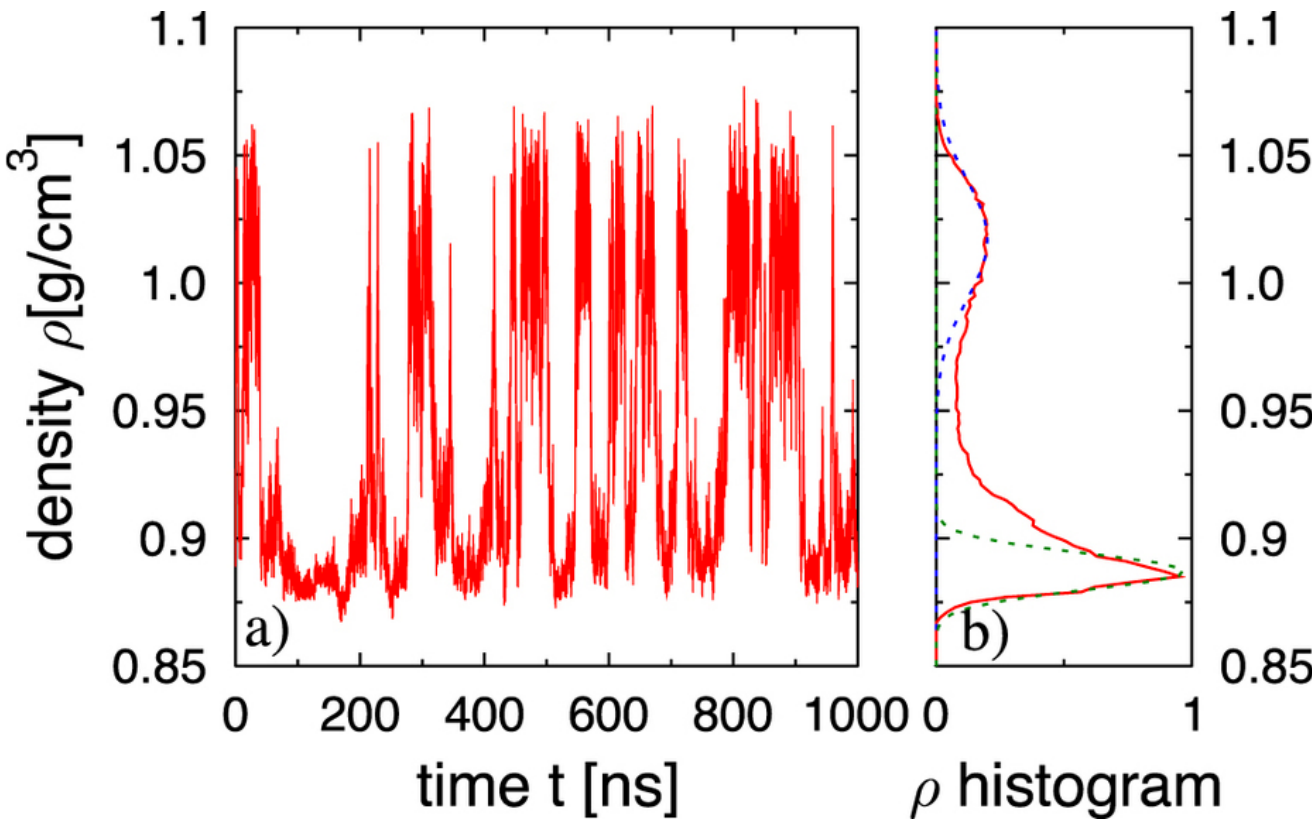
  thermal + phase + concentration fluctuations

Fluctuations between Two Liquid Phases of Water



A. Nilsson, L. G. M. Pettersson, *Nat. Commun.* 6, 8998 (2015).

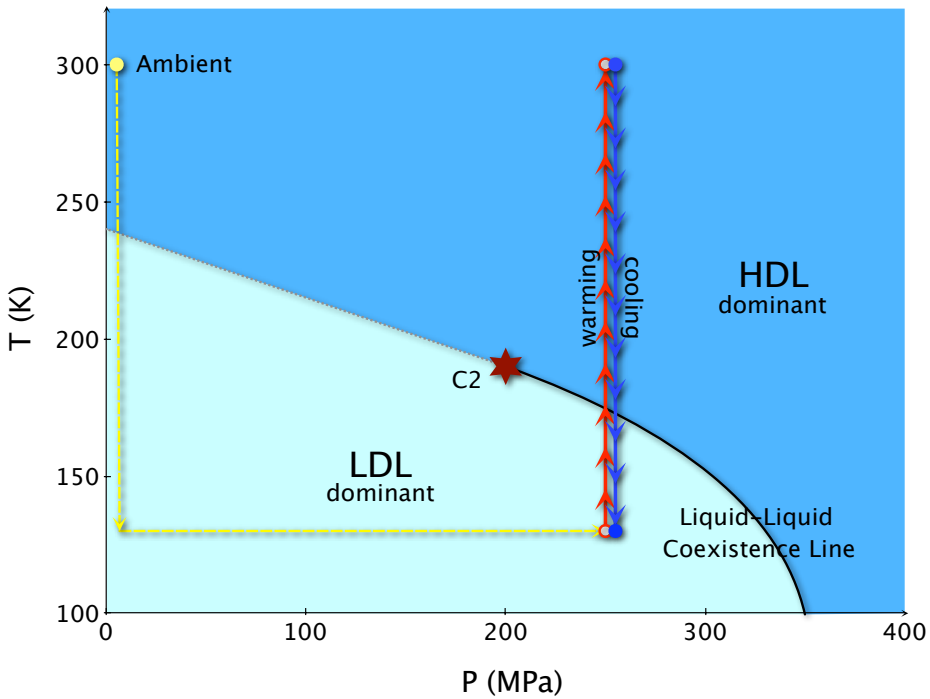
Nanoscale Dynamics of Phase Flipping

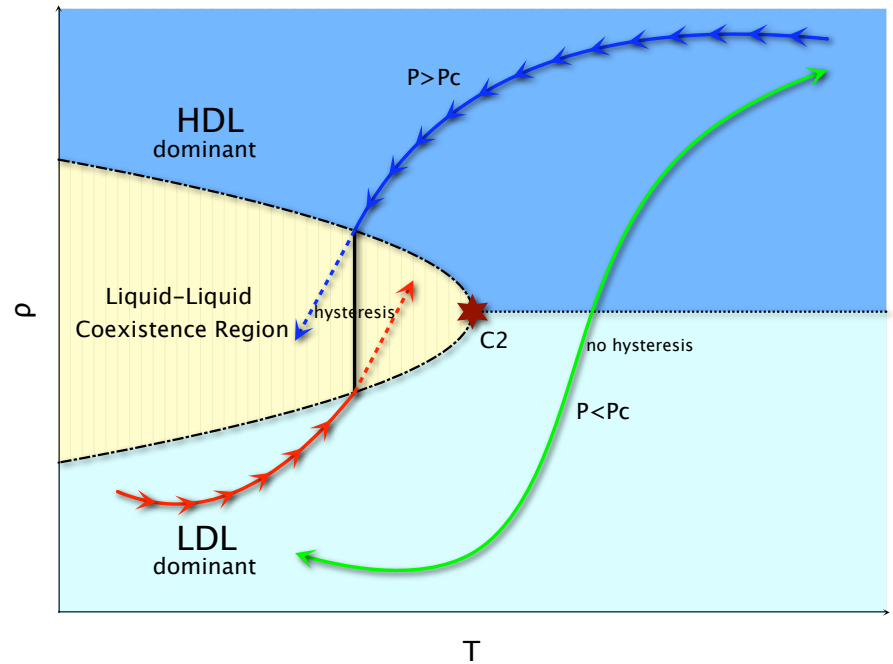


(a) The 1 μs time series shows how frequently, at constant $P = 215$ MPa and $T = 244$ K, $N = 343$ ST2-water molecules switch from LDL-like to HDL-like states. (b) The histogram for the sampled density values, in arbitrary units, after discarding the first 100 ns of the 1 μs time series. For LDL-like states $\rho \approx (0.89 \pm 0.01)$ g/cm^3 and for HDL-like states $\rho \approx (1.02 \pm 0.03)$ g/cm^3 corresponding to a difference of $\approx 13\%$ in density. Dashed lines are Gaussian best fits of the histogram around the two maxima.

T. A. Kesselring, G. Franzese, S. V Buldyrev, H. J. Herrmann, H. E. Stanley, *Sci. Rep.* 2, 474 (2012).

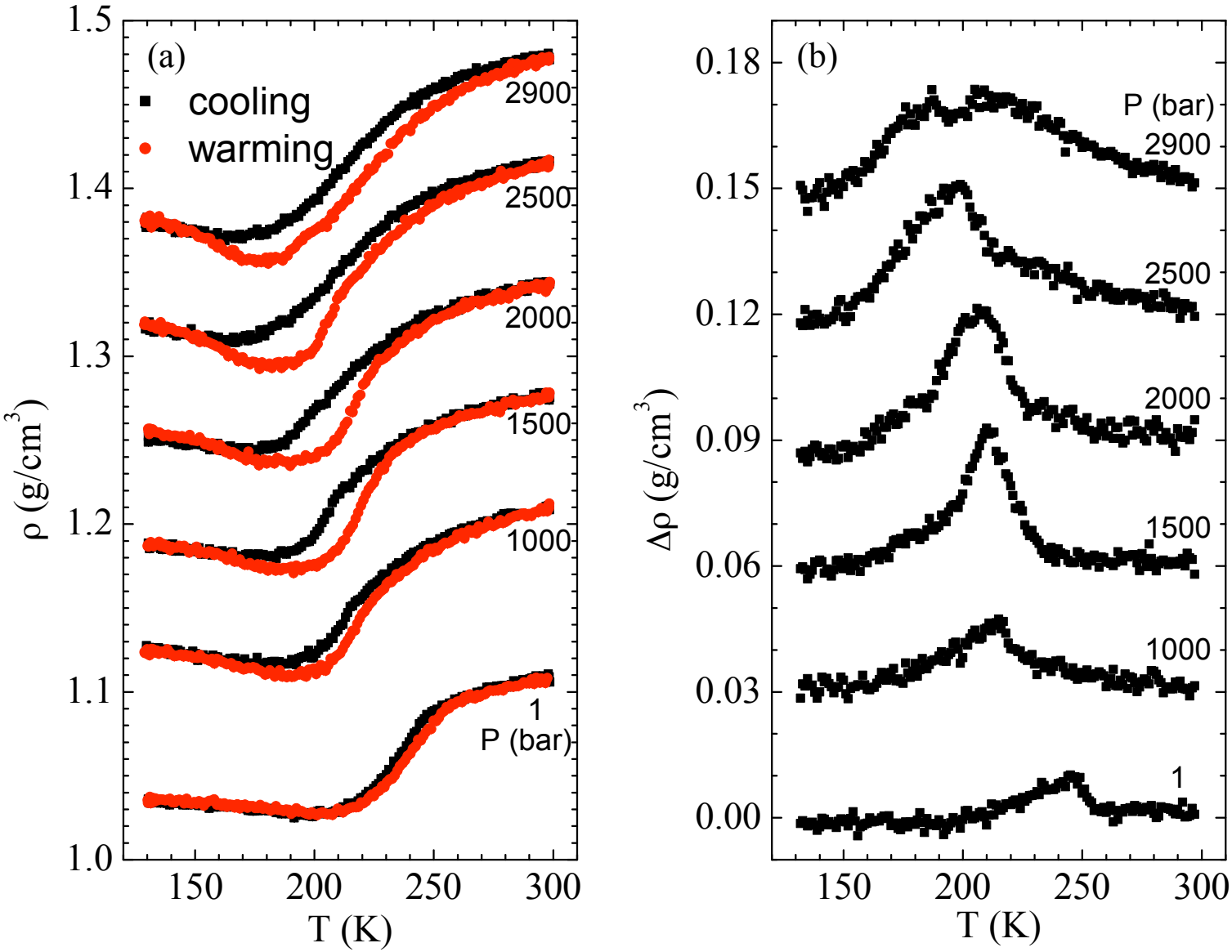
Bias the Density Fluctuations



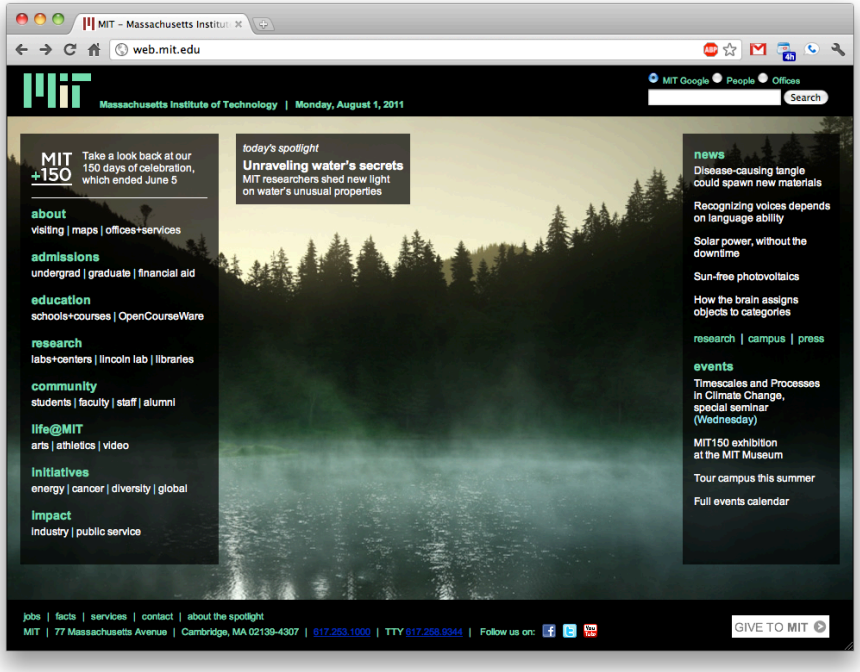


Y. Zhang, A. Faraone, **W. A. Kamitakahara**, et al., *PNAS* 108, 12206 (2011).

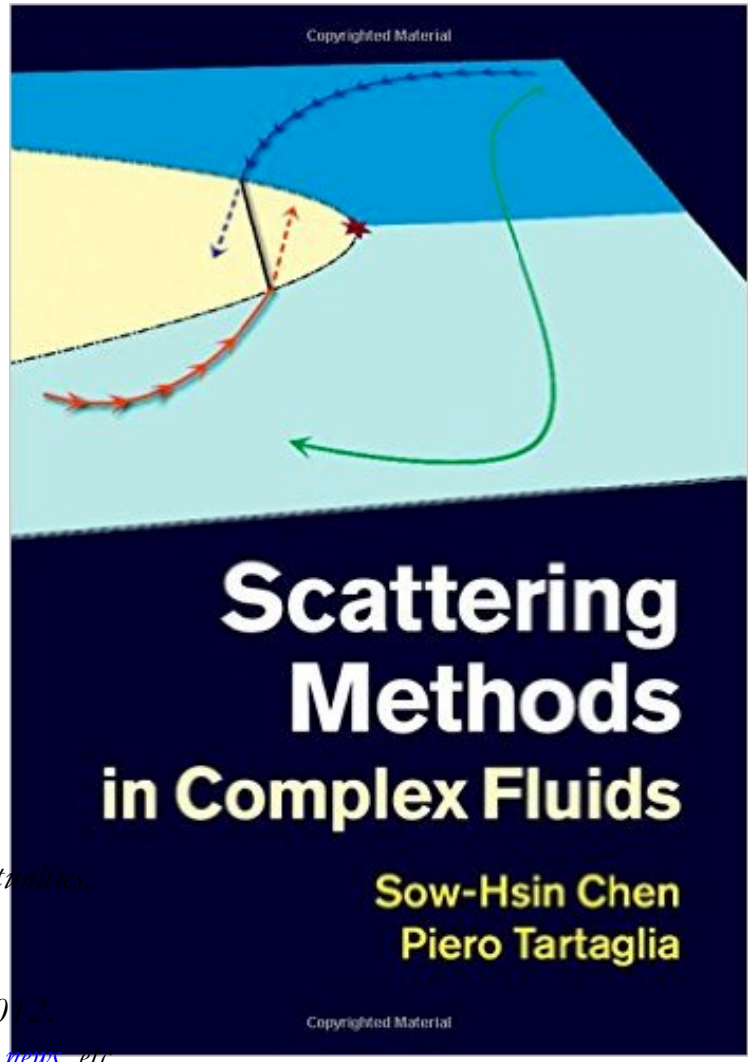
Evidence of a 1st-order Liquid-Liquid Phase Transition



Y. Zhang, A. Faraone, **W. A. Kamitakahara**, et al., *PNAS* 108, 12206 (2011).



MIT homepage, today's spotlight,
"Unraveling water's secrets", Aug. 1, 2011



"Density Hysteresis in Nanoconfined Water", 2011 Accomplishments and Opportunities, NIST Center for Neutron Research (2011).
"Shedding light on water's mysterious behavior", DOE Office of Science headlines.
Cover of the DOE Neutron Scattering Principal Investigators' Meeting Report, 2012.
"Revealing water's secrets", MIT news, MIT NSE news, Phys.org, ORNL in the news, etc.
"MIT research supports controversial theory about water", Newsroom America.
"MIT Scientists Tackle Water Controversy", Crazy Engineers.
"Explaining some of water's mysteries", Softpedia.
"The Secrets of Water", Hydrophilia.
"Water's secrets revealed", R&D Magazine.
"More light on anomalous behavior of water", Chemical Industry Digest.

Chosen as the cover figure of a milestone book
"Scattering Methods in Complex Fluids",
Cambridge University Press (2015)

- Liquid Rubidium:

  thermal fluctuations

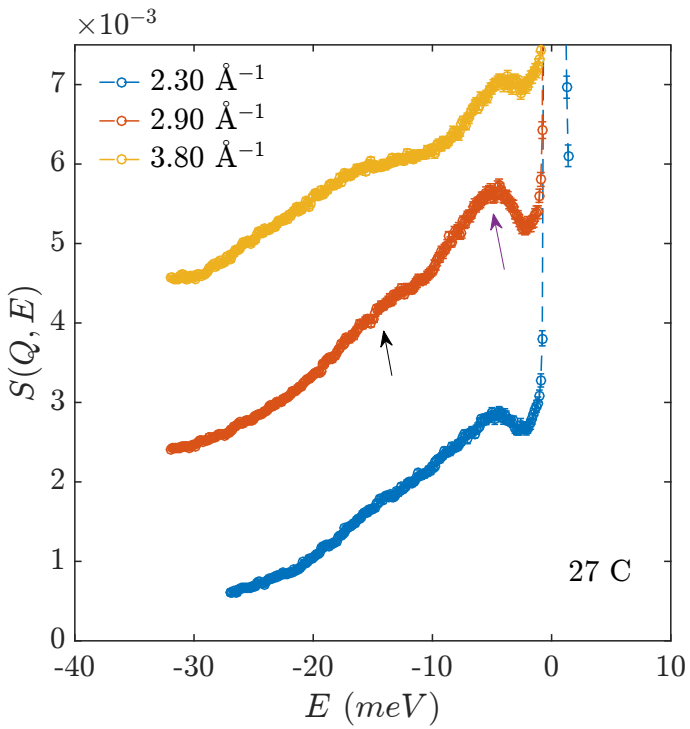
- Water:

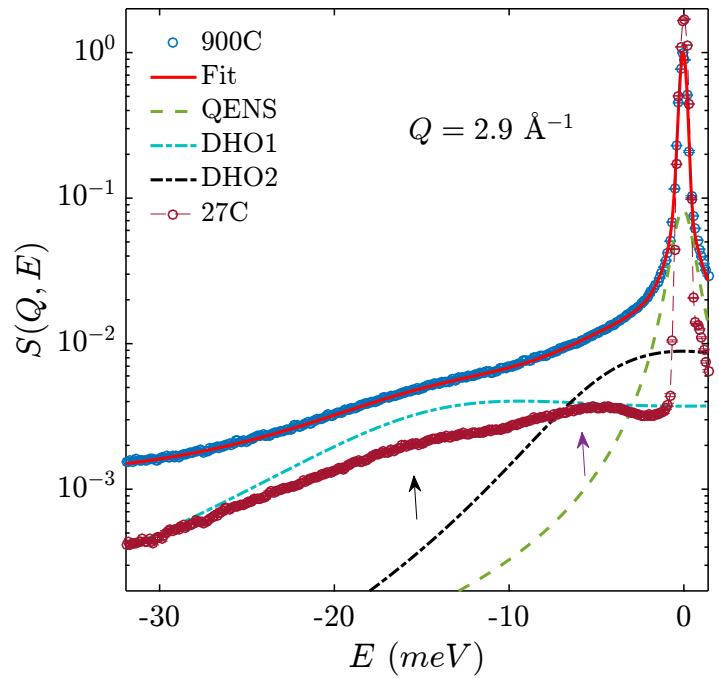
  thermal + phase fluctuations

- Glass-Forming Metallic Liquids:

  thermal + phase + concentration fluctuations

Melted Metallic Glass LM601 (CuZrNiAl)



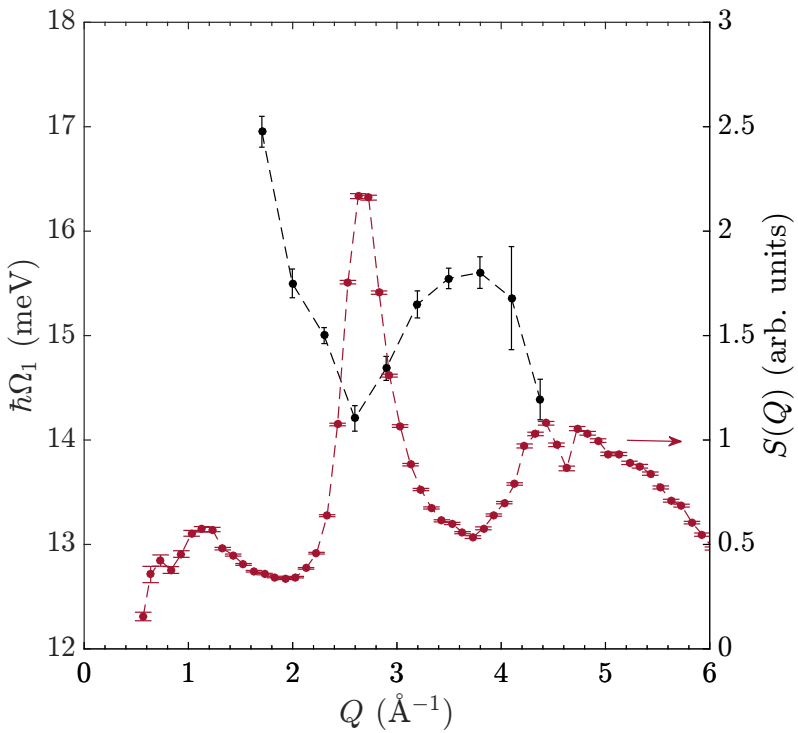


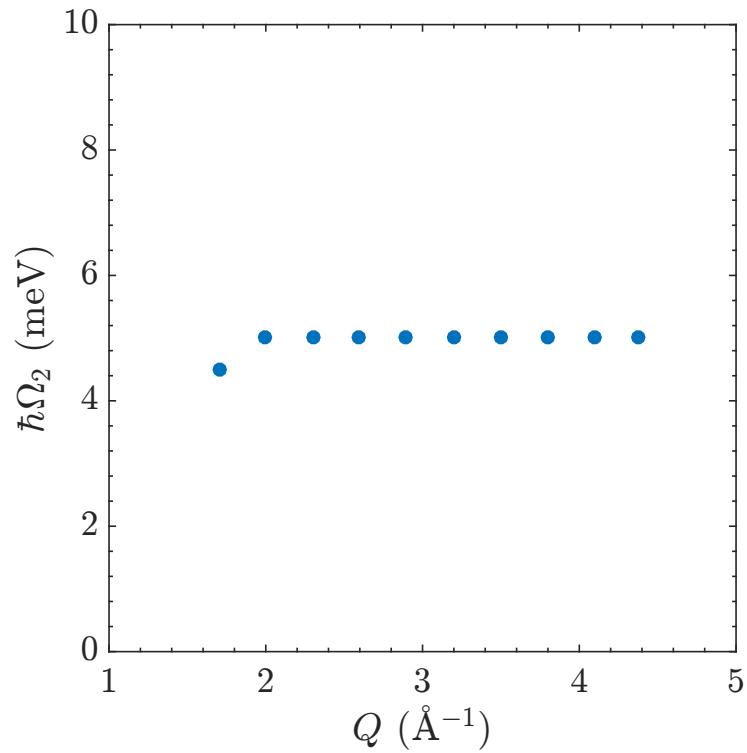
- Low Q challenging
- Viscoelasticity
- Entropy and Pressure fluctuations

to be published.

Dispersion of Two Excitations

- High energy excitation follows 1/S(Q)
- Low energy excitation is fixed to a constant energy value derived from Room Temperature data

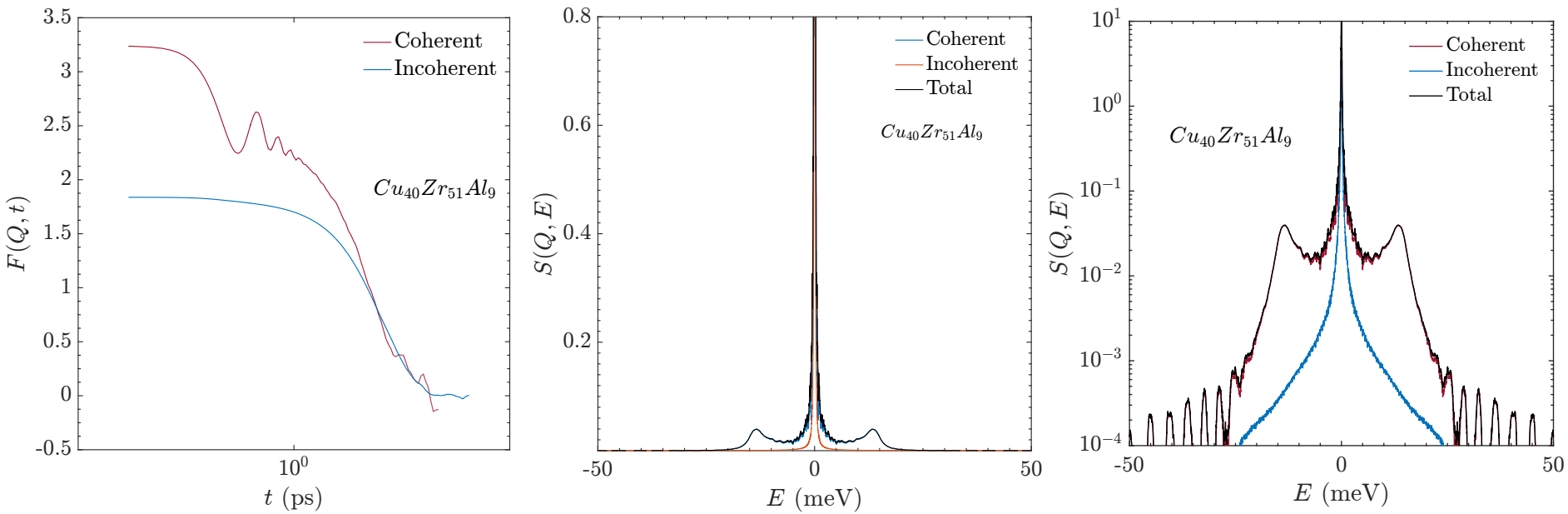




- highly localized

to be published.

Comparisons of Coherent and Incoherent Scattering (Q = 0.53 Å^{-1})



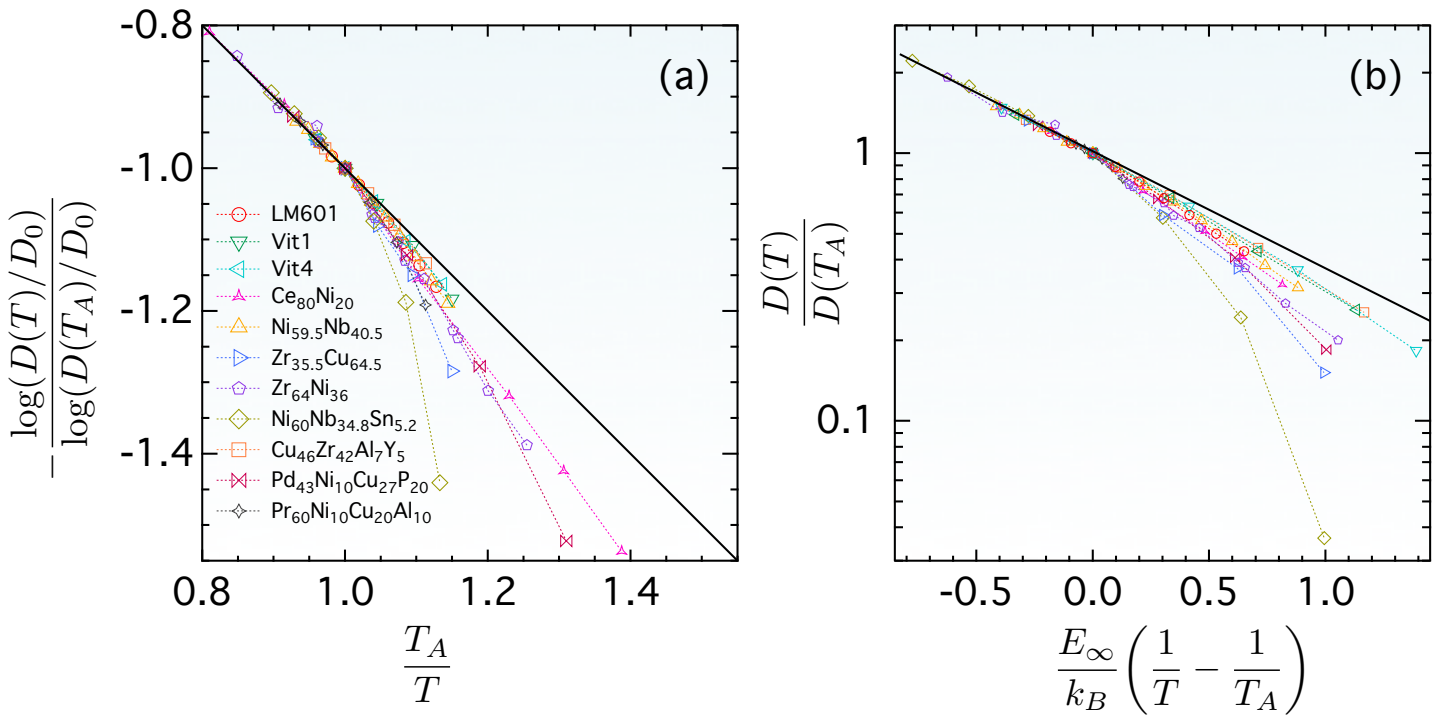
- effect of concentration fluctuation

to be published.

'Universality' of Arrhenius Crossover in Metallic Liquids

- High temperature Arrhenius behavior of 11 metallic liquids (experiments) show consistent deviation at $2T_g$
- Two different scaling:

$$\frac{D(T)}{D_0} = \exp\left(\frac{-E_\infty}{k_B T}\right) \Rightarrow \frac{\log(D(T)/D_0)}{\log(D(T_A)/D_0)} = \frac{T_A}{T} \qquad \frac{D(T)}{D(T_A)} = \exp\left(\frac{-E_\infty}{k_B}\left(\frac{1}{T} - \frac{1}{T_A}\right)\right)$$

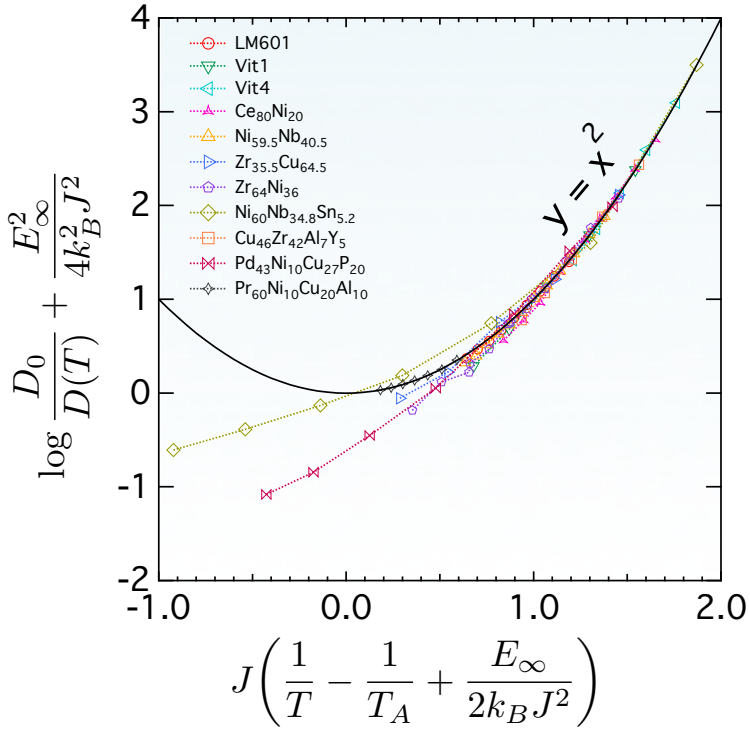


Submitted.

Parabolic Scaling below T_A

- Scaling of low temperature data using a parabolic form reveals consistent T_A

$$\frac{D_0}{D(T)} = \exp\left(J^2\left(\frac{1}{T} - \frac{1}{T_A}\right)^2 + \frac{E_\infty}{k_B}\left(\frac{1}{T} - \frac{1}{T_A}\right)\right)$$



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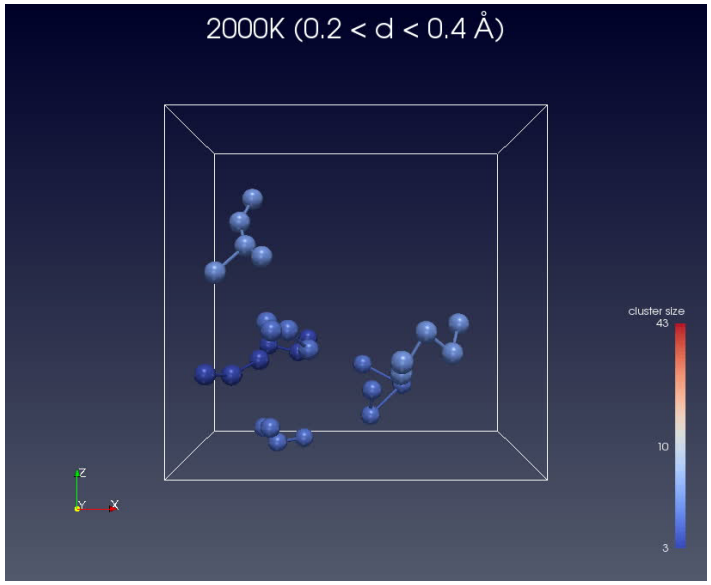
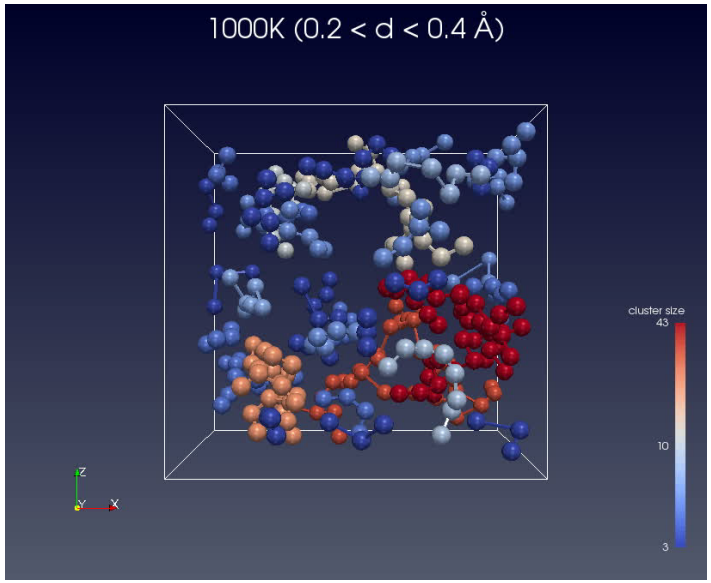
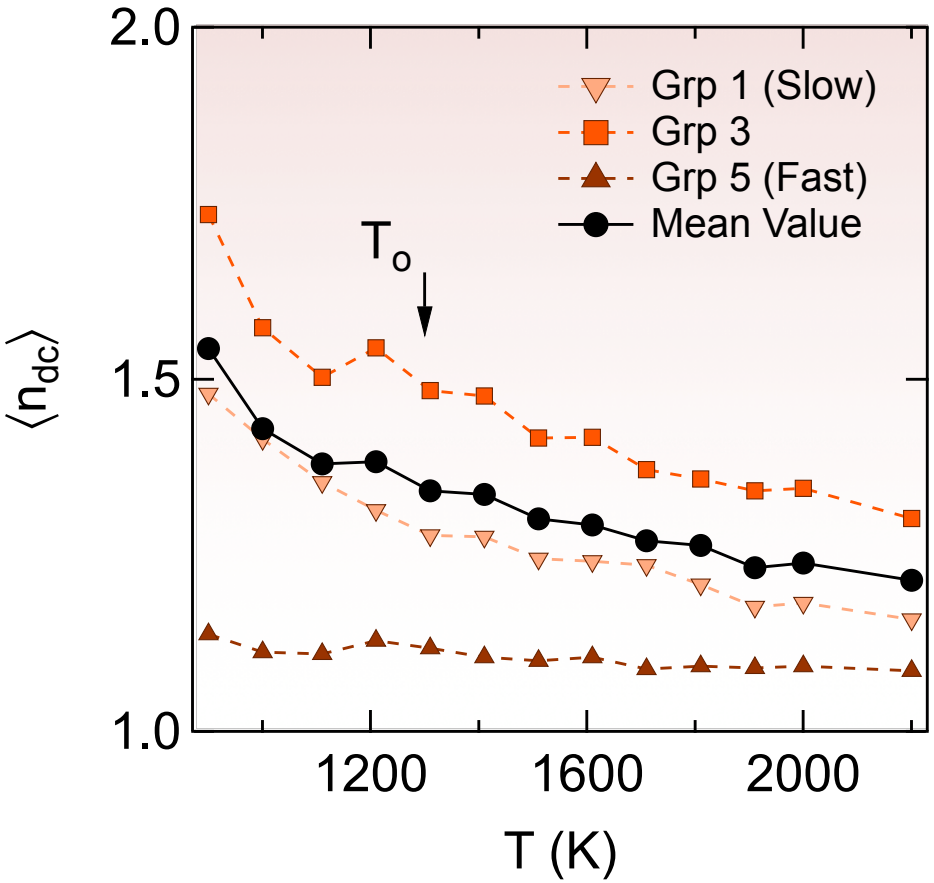
Dynamical Clustering, Machine Learning Analysis







Phys. Rev. B 91, 134204 (2015)
Phys. Rev. B 92, 024202 (2015)
J. Phys. Chem. B, in press
MRS Advances, in press

Dynamical Clustering

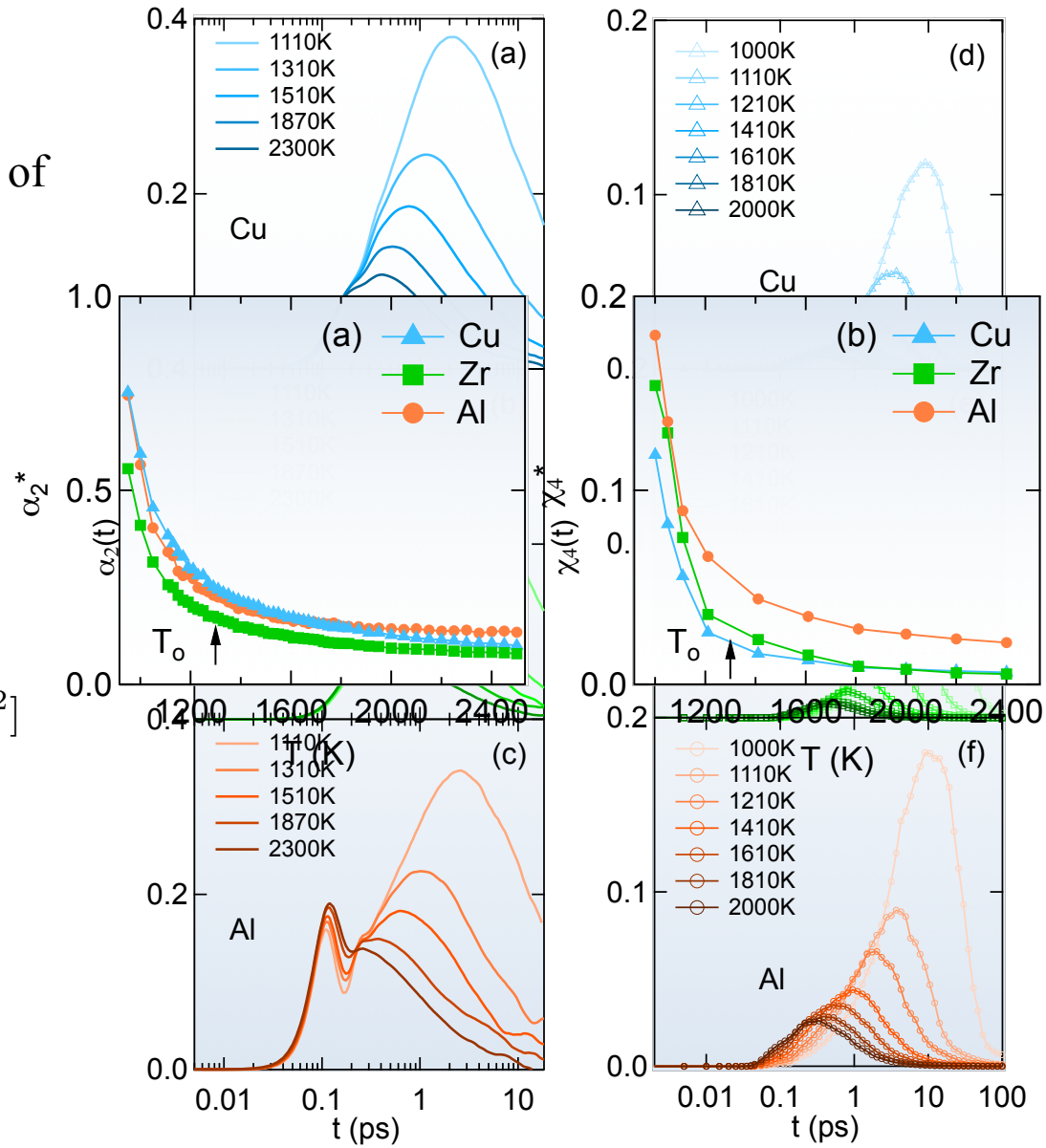
- Agrees with quantitative measures of dynamical heterogeneity
- Non-Gaussian parameter

$$\alpha_2 = \frac{3\langle[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^4\rangle}{5\langle[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2\rangle^2} - 1$$

- Four-point correlation functions

$$\chi_4(t) = \frac{V}{TN^2}[\langle Q_s^2(t)\rangle - \langle Q_s(t)\rangle^2]$$

$$Q_s(t) = \sum_{i=1}^{N} w(|\mathbf{r}_i(t) - \mathbf{r}_i(0)|)$$



LiquidLib by Zhang-Group

zhang-group.github.io/LiquidLib/

LiquidLib

First time users please register at:

Register

Registered users can access LiquidLib with their GitHub accounts:

Download TAR

View On GitHub

This project is maintained by Zhang-Group

Hosted on GitHub Pages using the Dinky theme

LiquidLib

Introduction

`LiquidLib` is a post-processing tool for molecular dynamics simulations with the capabilities to compute quantities useful in studying liquids and glasses. This package has built in support to analyze LAMMPS, GROMACS, and VASP trajectory files. The new release (**v0.2**) can run on a single processor or a shared memory module with OpenMP support.

Capabilities

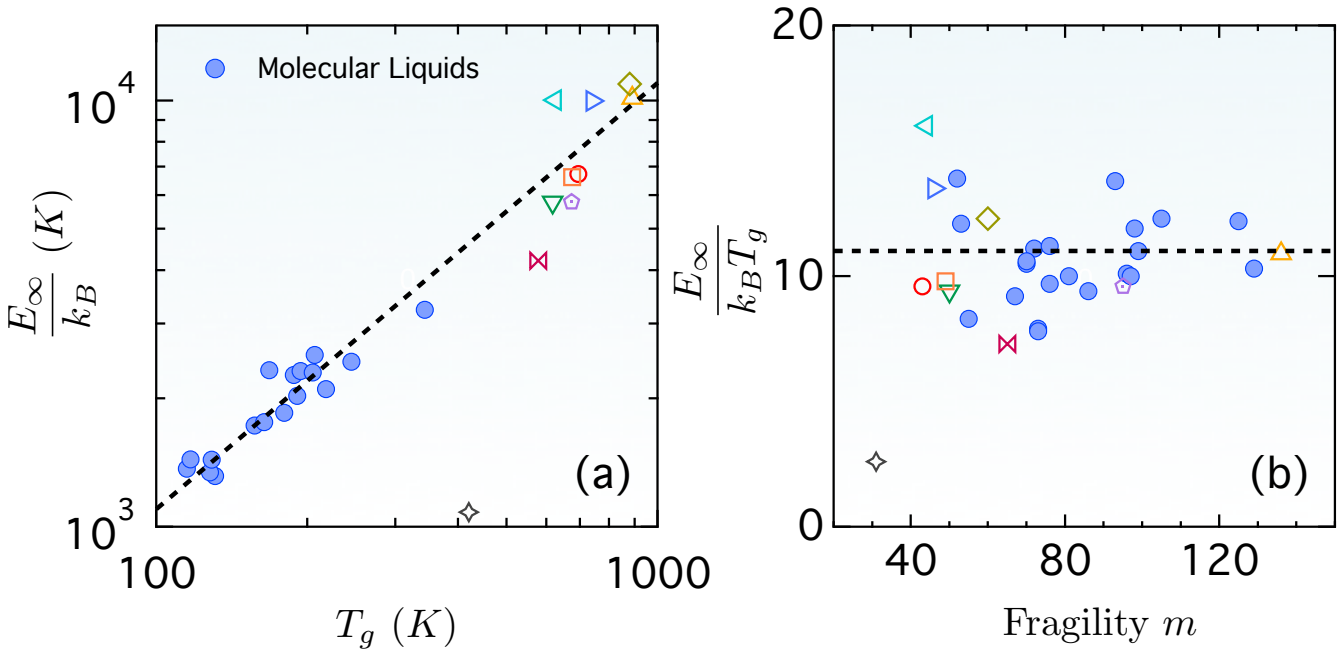
`LiquidLib` has the capabilities to compute the following quantities:

- Pair Distribution Function
- Structure Factor
- Mean Squared Displacement
- Non-Gaussian Parameter
- Four-point Correlation Function
- Velocity Auto Correlation Function
- Self van Hove Correlation Function
- Coherent van Hove Correlation Function
- Self Intermediate Scattering Function
- Coherent Intermediate Scattering Function

Uncorrelated reduced Activation Barrier

- Reduced E_∞ (scaled by $k_B T_g$) is same for molecular and metallic liquids irrespective of fragility m, and glass transition temperature T_g.

- Strong liquids: $E_\infty / k_B T_g \approx m$ (15 – 30)



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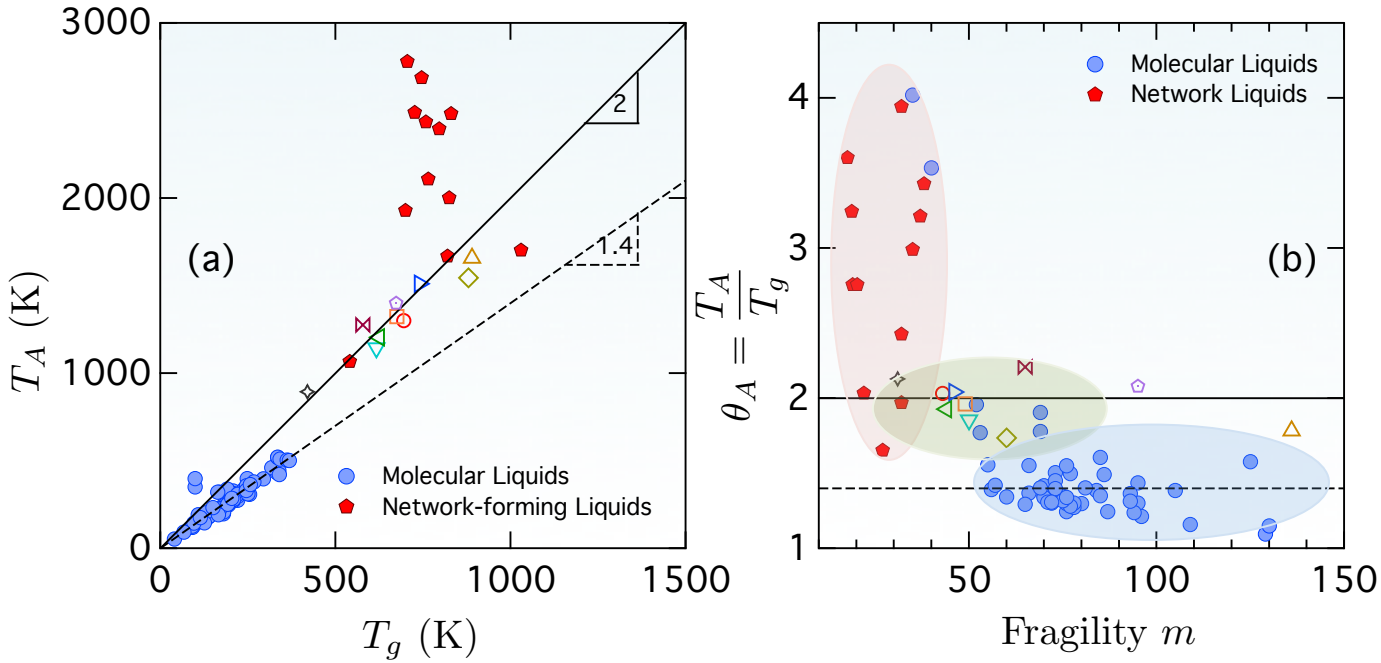
Correlation of Fragility with Arrhenius Crossover

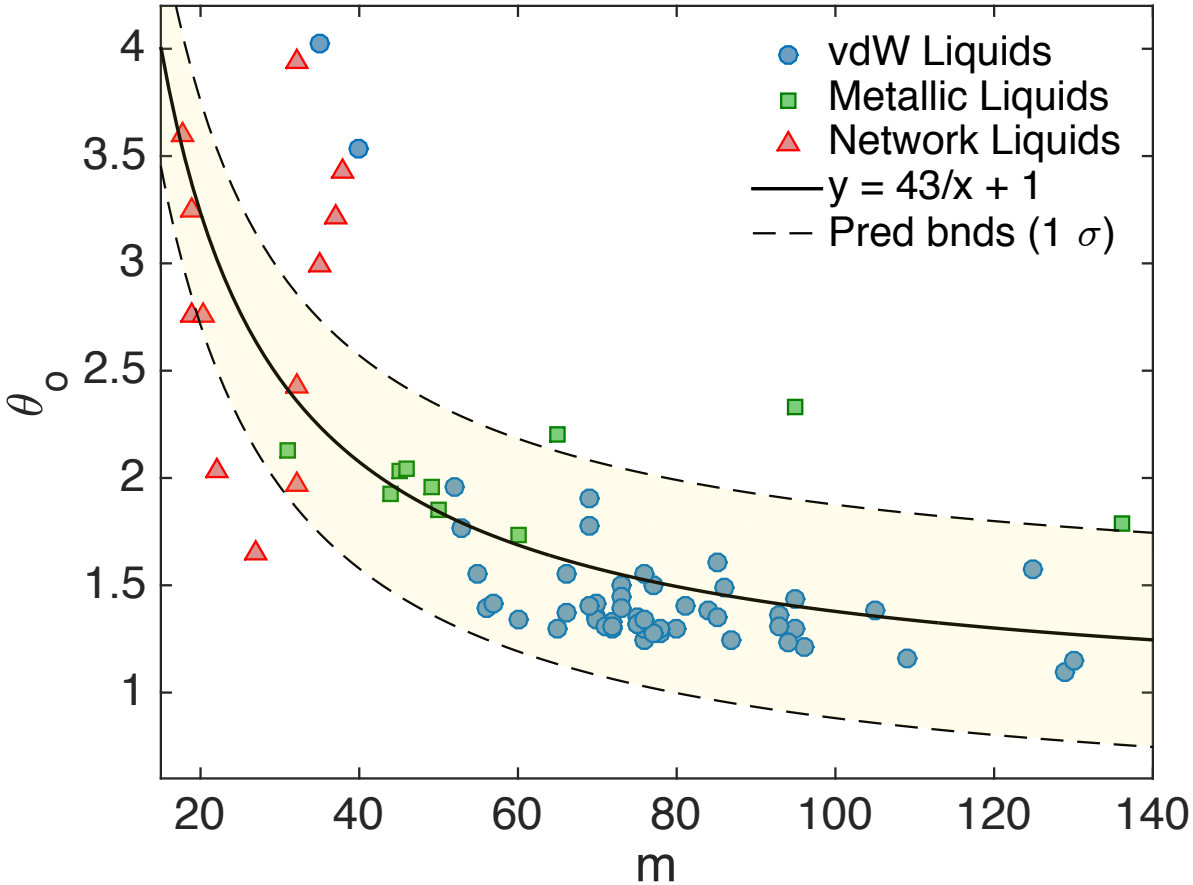
- $\theta_A = T_A/T_g$ vs m reveals 3 different regimes.
  - Metallic liquids: $T_A \sim 2T_g$ above T_m, and have intermediate fragility (40 – 60)
  - Molecular van der Waals liquids: $T_A \sim 1.4\ T_g$ usually below T_m, high fragility (50 – 150).
  - Network liquids: Strong behavior transpires into a wide range of T_A usually above T_m.



Submitted.

Correlation of Fragility with Arrhenius Crossover II

- Inverse correlation: $\theta_A = C/m + 1$



Submitted.

Congratulations to John, Bill, and David for their Outstanding Careers!

- Liquid Rubidium: **(John Copley)**

  thermal fluctuations

- Water: **(Bill Kamitakahara)**

  thermal + phase fluctuations

- Glass-Forming Metallic Liquids:

  thermal + phase + concentration fluctuations

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