Excess Entropy Scaling of Transport Properties of Liquids

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Overview

- Excess entropy scaling of transport properties of simple fluids (Rosenfeld, Dzugutov)
- Multiparticle correlation expansions of the excess entropy (Green)
- Liquids with Water-like Anomalies: Structure, entropy and transport relationships
- **Water models: TIPnP, SPC/E**
  Tetrahedral Ionic Melts: SiO_2, BeF_2, GeO_2
  Fluids with isotropic, core-softened interactions
  Patchy colloids
  Covalently bonded liquids: silicon, germanium etc
- Transition from stable to supercooled regime: Deviations from Rosenfeld-scaling behaviour

Rosenfeld Excess Entropy Scaling of Transport Properties of Simple Liquids

Links thermodynamic and transport properties

$$X^* = A\exp(\alpha S_e)$$

Scaling parameters for simple liquids (Hoover and others)

Diffusivity

$$D^* = D(\rho^{1/3} \big/ (k_B T / m)^{1/2}) = 0.6\exp(0.8 S_e / k_B)$$

Viscosity

$$\eta(\rho^{-2/3} \big/ (m k_B T)^{1/2}) = 0.2\exp(-0.8 S_e / k_B)$$

Thermal Conductivity

$$\kappa(\rho^{-2/3} \big/ k_B (k_B T / m)^{1/2}) = 1.5\exp(0.5 S_e / k_B)$$

Rosenfeld, Phys. Rev. A (1977), Chem. Phys. Lett. (1977) J. Phys. Cond. Matt. (1999)
Dzugutov, Nature (1996)

When and why does Rosenfeld-scaling work?

$$X^{*} = A\exp(\alpha S_e)$$

- Diffusion in liquids proceeds by binary collisions and cage relaxations.
- Binary collision component is taken care of by macroscopic reduction factor based on elementary kinetic theory. Assumes that you can assign an effective hard-sphere radius.
- Cage relaxation determined by excess entropy.
- Semiquantitative corresponding states type relation. Rosenfeld's arguments based on:

$$C(t) = \left\langle A^2 \right\rangle + (1/2)\left\langle A(0)\ddot{A}(0)\right\rangle t^2 + ...$$

- Justification based on mode-coupling theory (S. K. Ghosh (2001), S. P. Das (2001))

Energy landscape picture

$$\ln X^* = \ln A + \alpha S_e$$

- Connectivity of configurational states is very large in the liquid state. The probability that a particle will be able to move from its current position depends on the number of available configurational states i.e. exp(αS_e)
- The exponential scaling parameter α depends only on the nature of the interaction potential and is otherwise independent of state-point.
- Note the contrast with Adam-Gibbs scaling:

$$\ln D \propto -1/(TS_c)$$

As the liquid cools, configuration space connectivity should reduce, leading to departures from Rosenfeld-scaling.

Multiparticle Correlation Expansions of the Entropy

$$S = S_{id} + S_e = S_{id} + S_2 + S_3 + \dots$$

$$S_e \equiv \text{Thermodynamic excess entropy of the liquid}$$

$$S_n \equiv \text{n - particle correlation function contribution}$$

[Green(1952), Baranyai (1989)]

Monoatomic Fluid

$$S_{id}/(Nk_B) = \frac{5}{2} - \ln\left(\rho\Lambda^3\right)$$

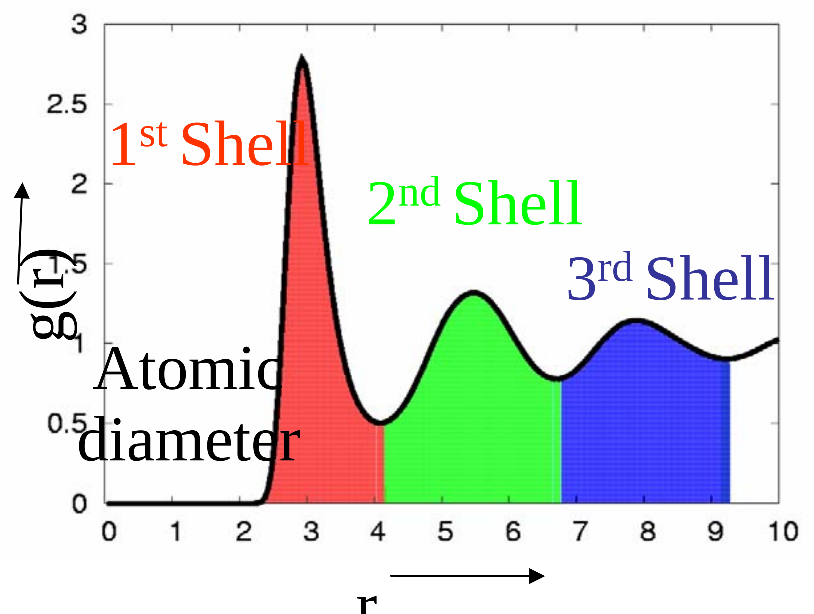
$$S_2/(Nk_B) = -2\pi\rho\int\left[g(r)\ln g(r) - g(r) + 1\right]r^2 dr$$

Pair Correlation Entropy:
A convenient structural estimator of the thermodynamic excess entropy

Pair approximation to entropy of a mixture of atomic species α and β with mole fractions χ_α and χ_β can be written in terms of atom-atom radial distribution functions

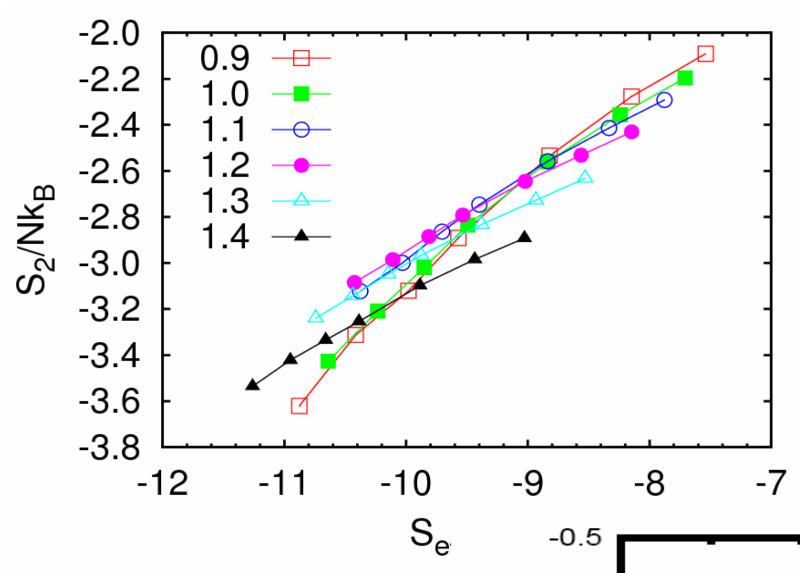
$$S_2 / Nk_B = -2\pi\rho \sum_{\alpha,\beta} \chi_\alpha \chi_\beta \int_0^\infty \{ g_{\alpha\beta}(r) \ln g_{\alpha\beta}(r) - [g_{\alpha\beta}(r) - 1] \} r^2 dr$$

- Accounts for 80-90% of the thermodynamic excess entropy
- Conveniently estimated from simulations and neutron diffraction experiments
- Easily related to calorimetric estimates of entropy

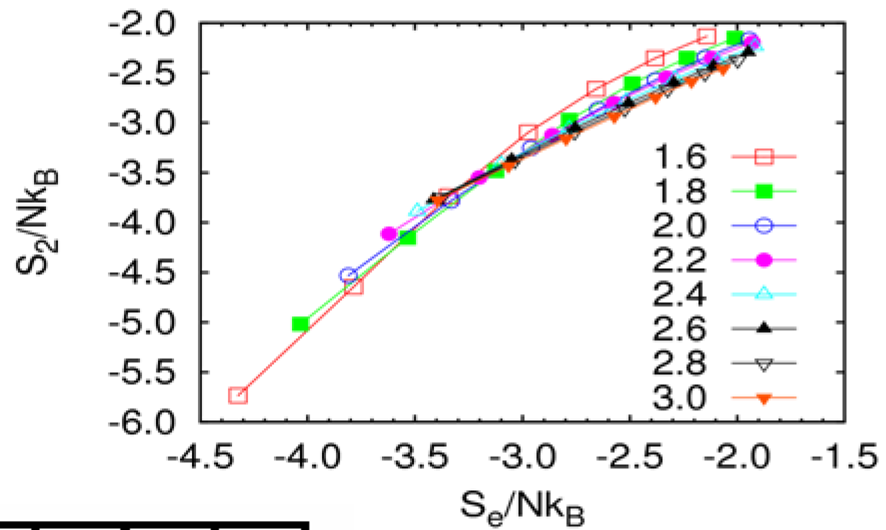


Using atom-atom RDFs to estimate Pair Entropy in Different Liquids

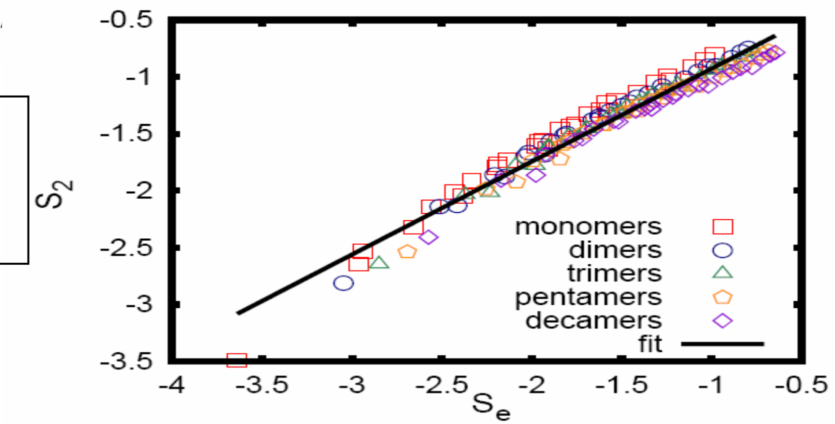
Molecular liquid: H_2O (SPC/E)



Ionic melt: BeF_2 (TRIM)



Lennard-Jones Chain fluids



Chakavarty et al

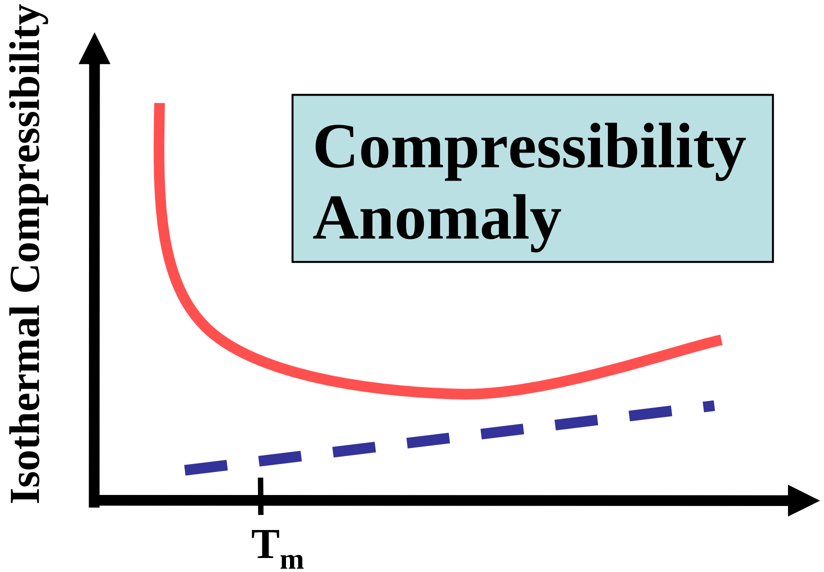
J. Chem. Phys. (2008)

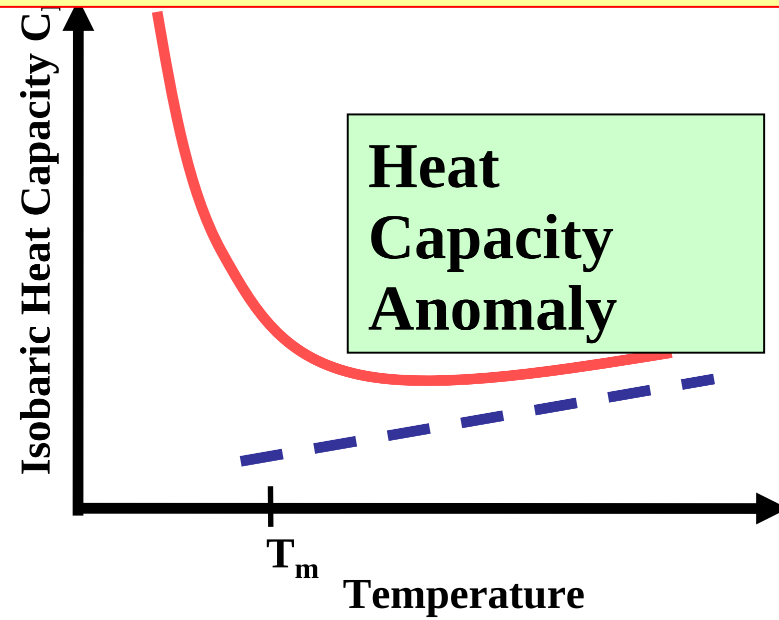
Mol.Phys. (2008)

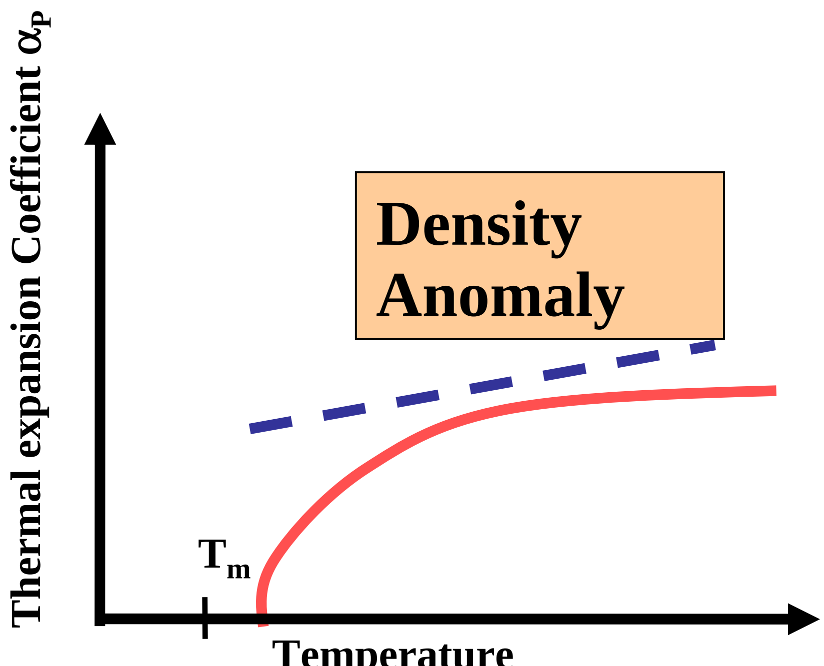
J. Phys. Chem. B (2009)

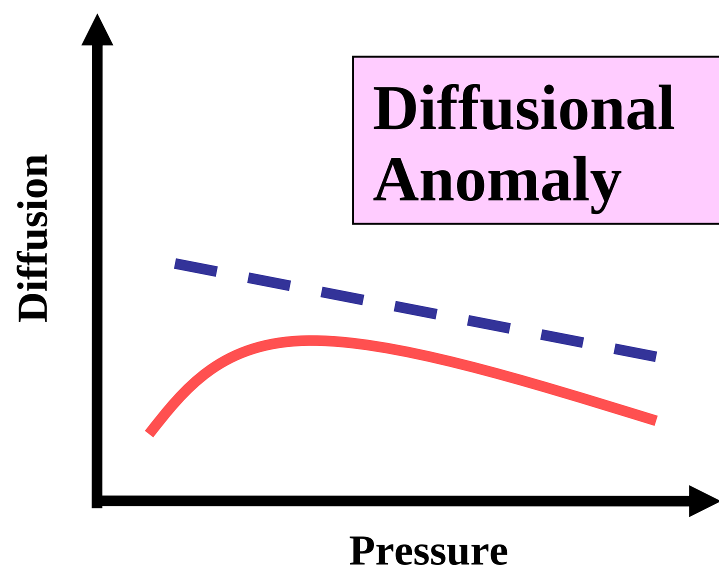
Water

Thermodynamic and Kinetic Anomalies of Water









Hydrogen-bonding in Water

Tetrahedral H-bonding

• Anisotropic hydrogen bonds which impose local tetrahedral order

• Each water can form 4 hydrogen bonds

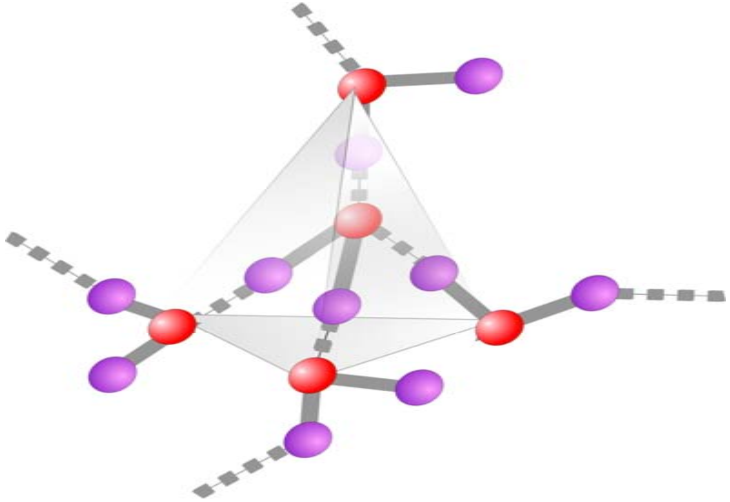
  3-dimensional network

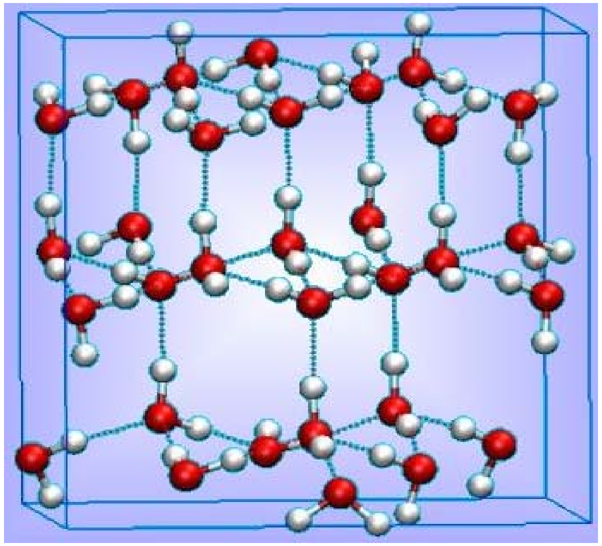
• Hydrogen bond energy: 5 – 10 kT

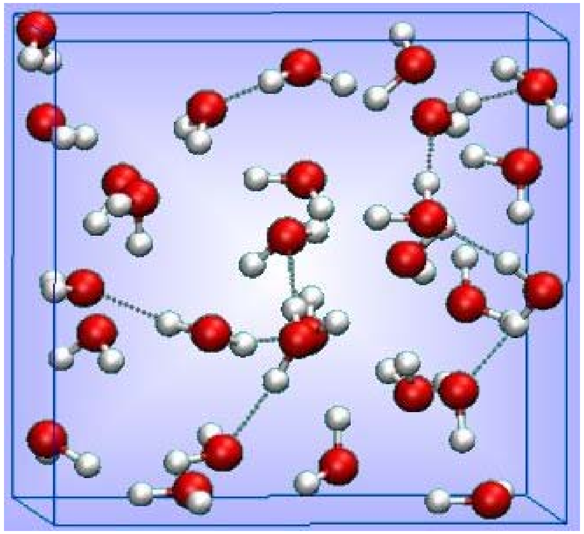
  Fluctuating network

• Basic structural unit: the Walrafen pentamer

• Assumed to underly anomalies and hydrophobic effect







Quantifying Order in Liquids

Short-range translational order parameter/density-induced ordering: measures extent of pair correlations.

$$\tau = \frac{1}{\xi_c}\int_0^{\xi_c}\left|g(\xi) - 1\right| d\xi,$$

(Debenedetti, Torquato)

Local bond orientational order parameters: sensitive to local isosahedral order in simple liquids.
Average value of spherical harmonic of order *(l,m)* taken over 12 nearest neighbours is included in the sum over *m.*

$$Q_l = \left[\frac{4\pi}{(2l+1)}\sum_{m=-l}^{l}\left|\overline{Y_{lm}}\right|^2\right]^{\frac{1}{2}}$$

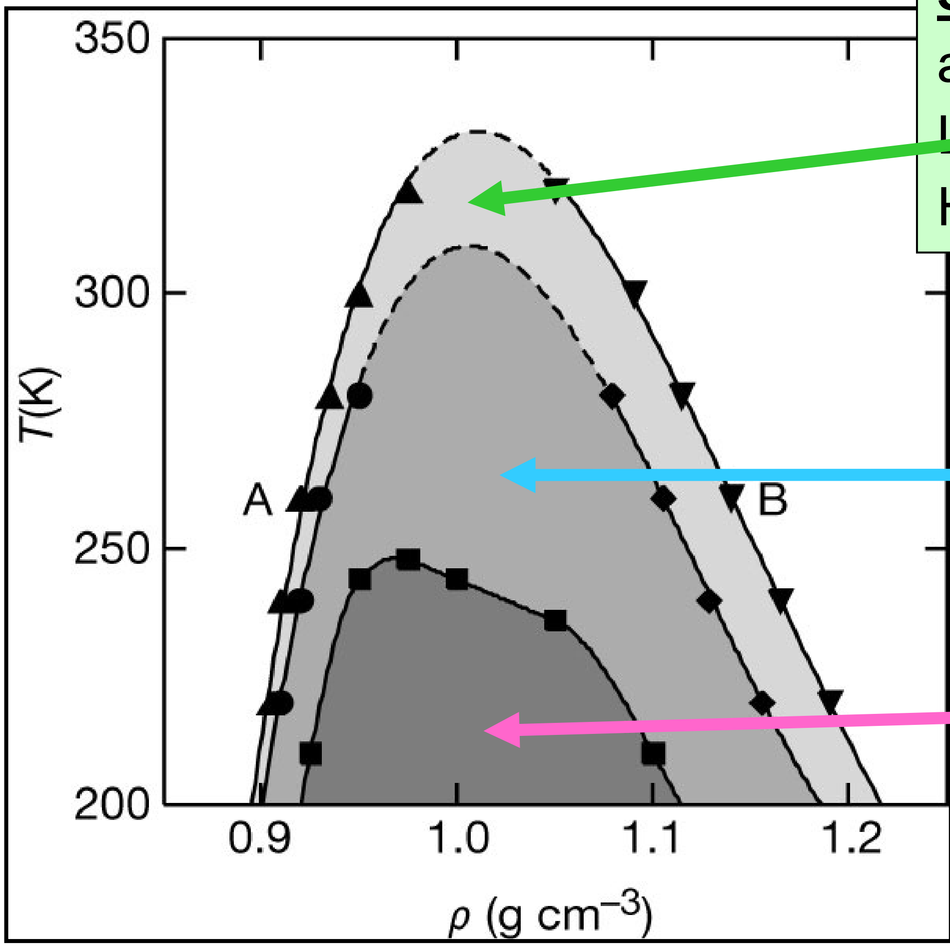
(Steinhardt & Nelson)

Local tetrahedral order parameter tendency of four nearest neighbors to adopt a tetrahedral configuration around an atom

(Chau & Hardwick)

$$q_{tet,A} = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\psi_{jk} + \frac{1}{3}\right)^2$$

Nested Structure of Anomalous Regions



Structural anomaly: Orientational and translational order are correlated
Low density boundary: maxima in q_{tet}
High density boundary: minima in

Diffusional anomaly: Bounded by loci of maxima and minima in self-diffusivity coefficients, for which $(dD/d\rho)_T > 0$

Thermodynamic anomaly: region where $(d\rho/dT)_P > 0$.

Errington and Debenedetti, Nature (2001)

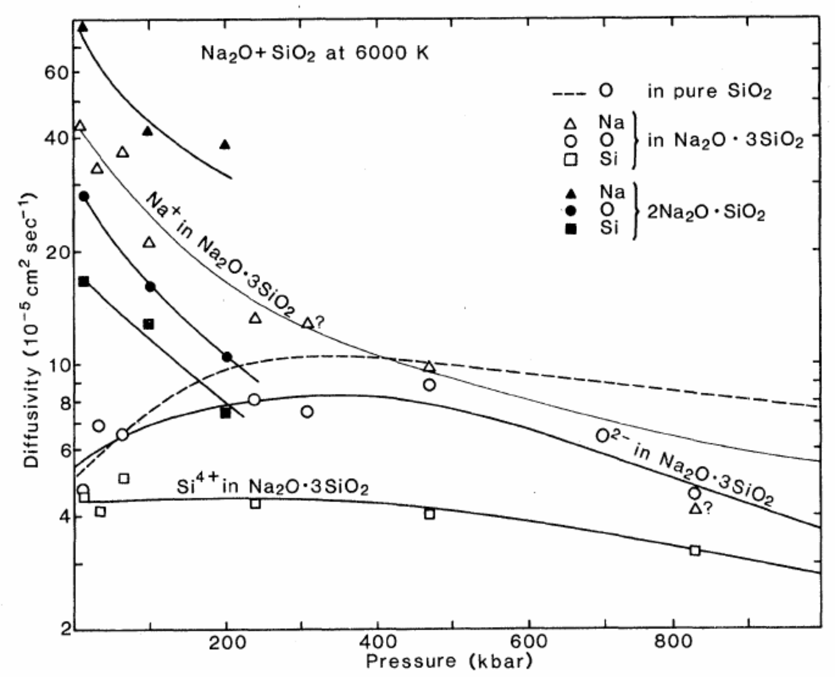
Liquids with Water-like Anomalies

AB_2 Tetrahedral Ionic Melts

Ionic melts with partial covalent character : covalency implies anisotropic bonds with open random network. Even within an ionic model, Pauling's radius ratio rules impose tetrahedral local order.

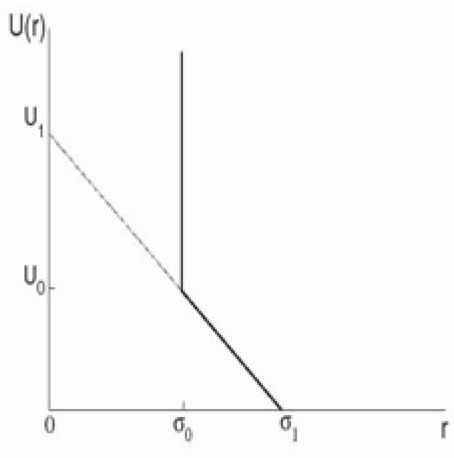
AB_2	Angle ABA	T_m(K)	r_+/r_-
H_2O	≅173°	273	-
BeF_2	≅150°	813	0.32
SiO_2	≅150°	1996	0.37
GeO_2	≅ 130°	1389	0.43

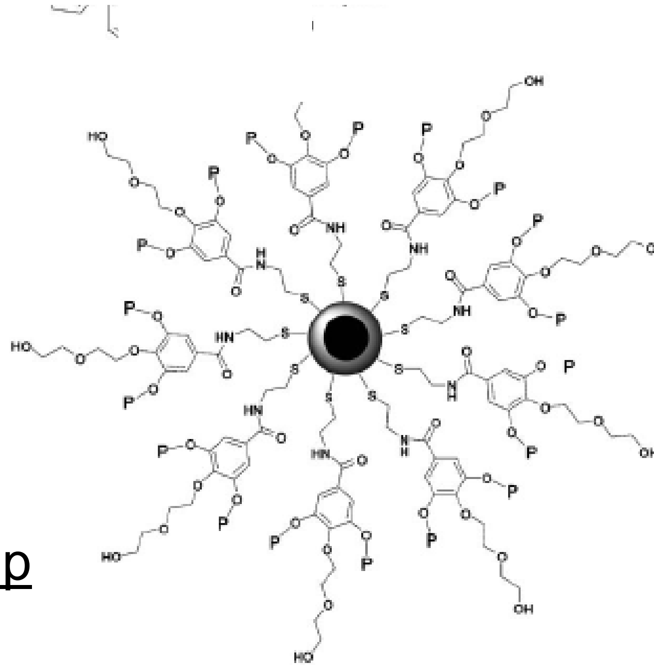
Angell, Science (1976 & 1982)



0.225 < Tet. Co. < 0.414

Liquids with Waterlike Anomalies: Mesoscopic Fluids with Core-softened Interactions





- Capped nano-particles
- Star Polymers
- Colloid-polymer mixtures

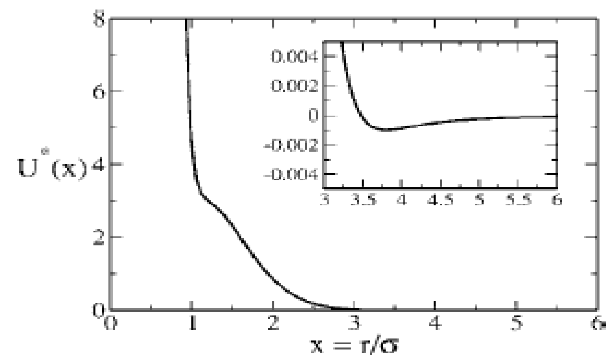
<u>2-scale linear ramp</u>

Jagla, Phys. Rev.

Stanley et al

<u>Lennard-Jones + Gaussian</u>

de Oliveira et al,
J. Chem. Phys (2006)



$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + a\epsilon \exp\left[-\frac{1}{c^2}\left(\frac{r-r_0}{\sigma}\right)^2\right]$$

Computational Details

Molecular Dynamics

- Potentials
  - Water : SPC/E, TIPnP
  - Silica : modified BKS
  - BeF_2 : TRIM
- Cubic boundary conditions:
- System size
  - Water : 256 molecules
  - Silica : 150 Si and 300 O ions
  - BeF_2 : 150 Be and 300 F ions
- Ensemble: Canonical (*N*-*V*-*T*)
- MD Code: DL_POLY package, 1fs timestep, leap-frog Verlet, Berendsen thermostat

- Long-range electrostatic interactions:
  Ewald Summation
- Diffusivity
  Einstein relation
- Viscosity/Ionic conductivity
  Green-Kubo relation
- Entropy: Thermodynamic integration

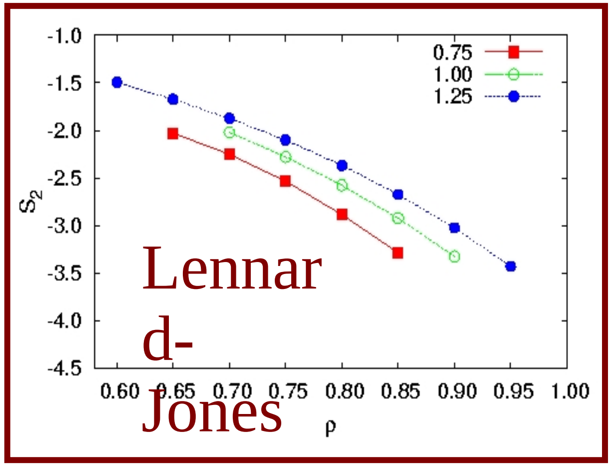
Monte Carlo

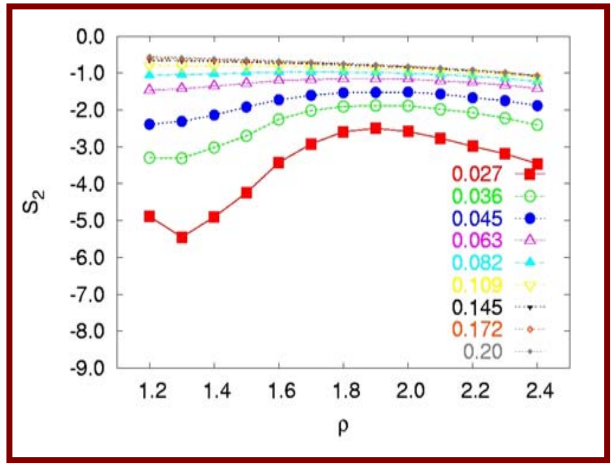
Potentials
Two-scale ramp
Periodic boundary conditions:
Cubic/256 molecules
Ensemble:
Canonical (*N*-*V*-*T*)

Excess/Pair Entropy Anomaly

Simple Liquids: S_2 is a monotonically decreasing function of density

Liquids with water-like anomalies: S_2/Se shows clear minimum, followed by maximum





2-scale ramp

Sharma, Chakraborty & Chakravarty

J. Chem. Phys. (2006)

$$S = S_{id} + S_{ex}$$

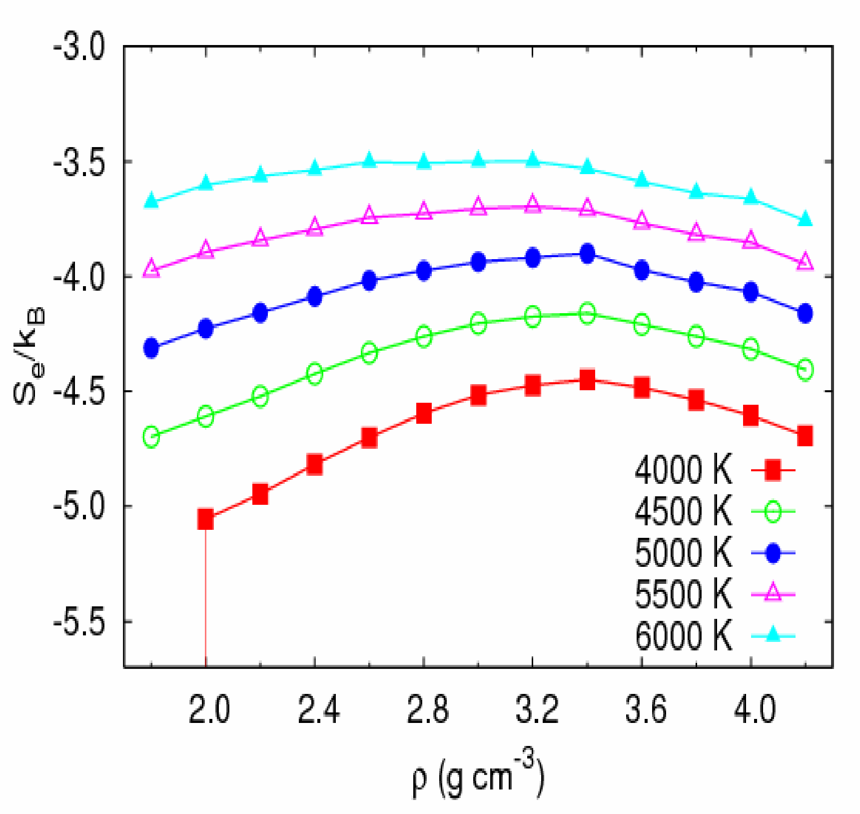
$$S_{id} / Nk_B = 1 + \sum_m x_m \left(1.5 - \ln\left(\rho_m \Lambda_m^3\right)\right)$$

$$\left(\frac{\partial S}{\partial \rho}\right)_T = V^2 \frac{\alpha}{\kappa} = 0 \Rightarrow \alpha = 0$$

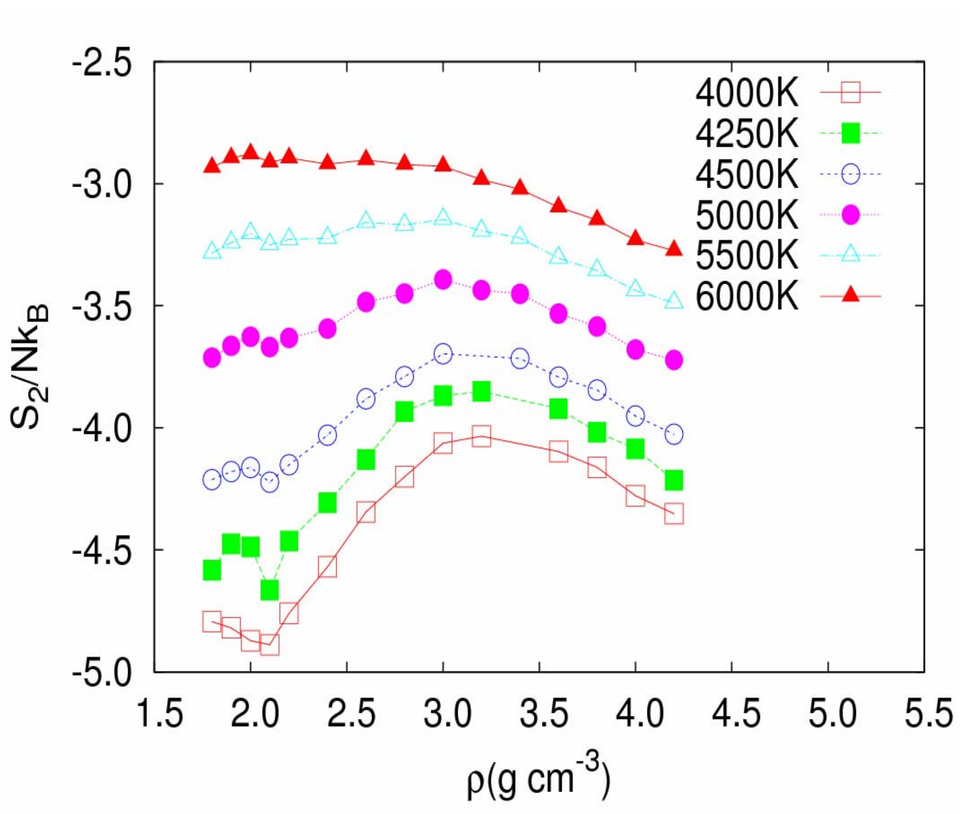
Existence of an excess entropy anomaly must imply a density anomaly i.e. a set of state points for which density increases on isobaric heating

Excess/Pair Entropy Anomaly in molten Silica

S_e

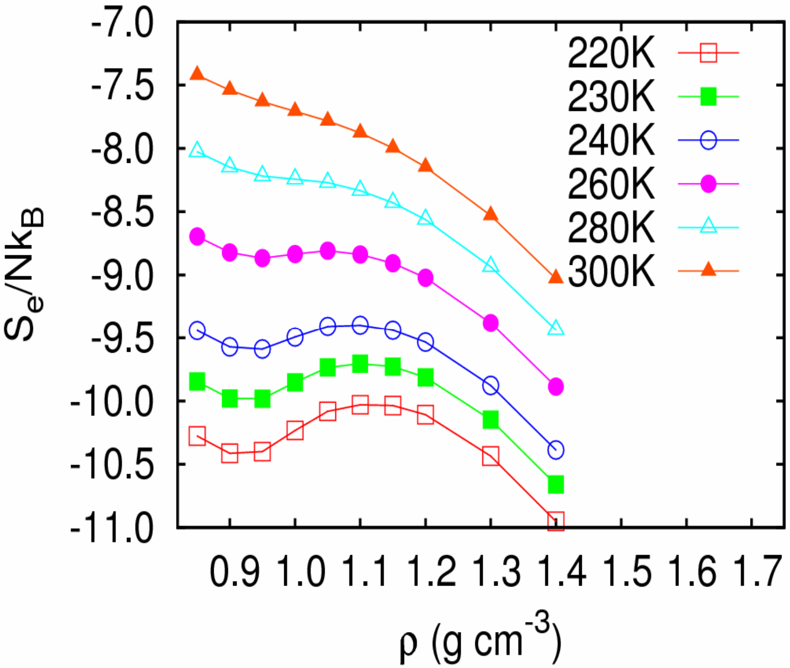


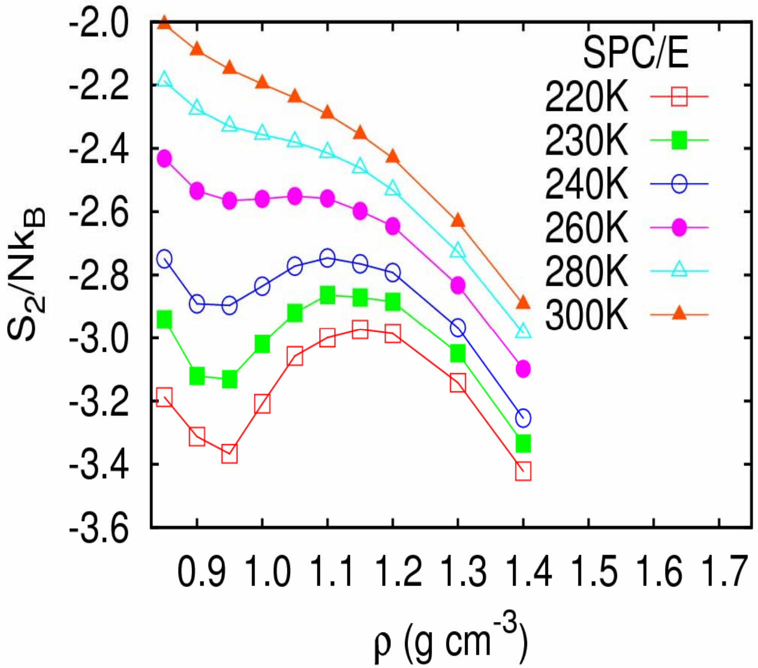
S_2



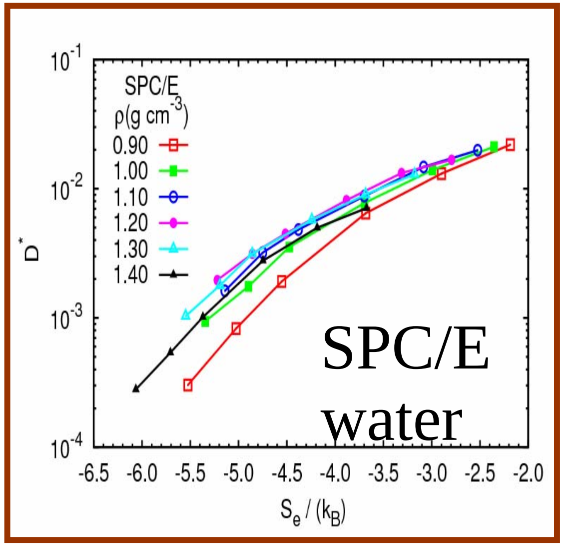
Excess/Pair Entropy Anomaly in the SPC/E Model of Water

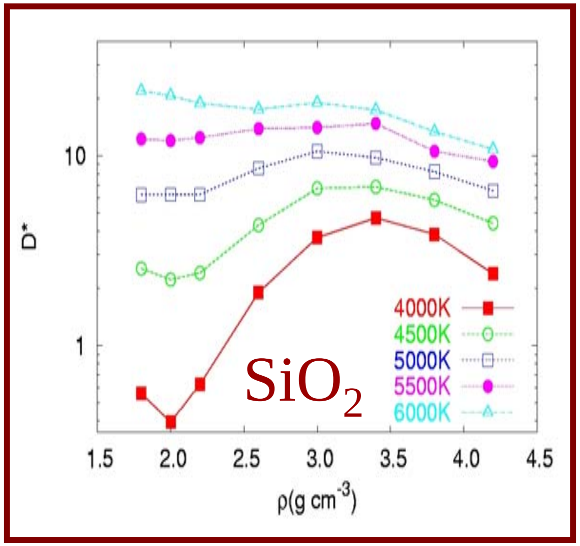
S_e S_2





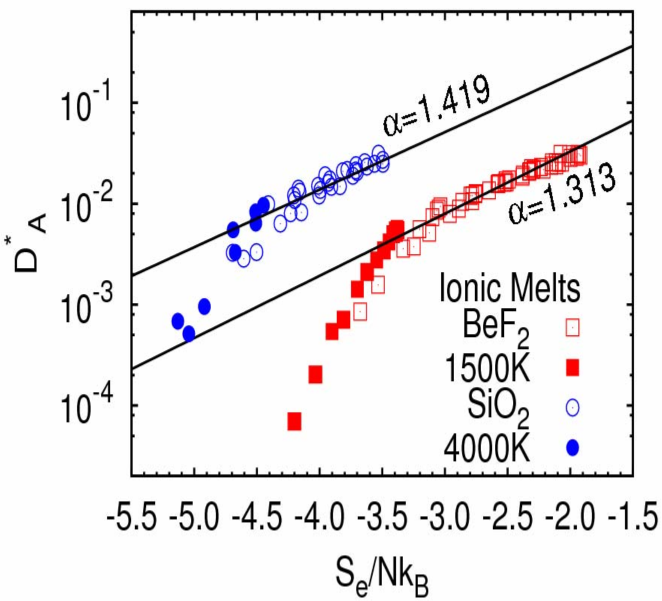
Excess Entropy Scaling of Diffusivities

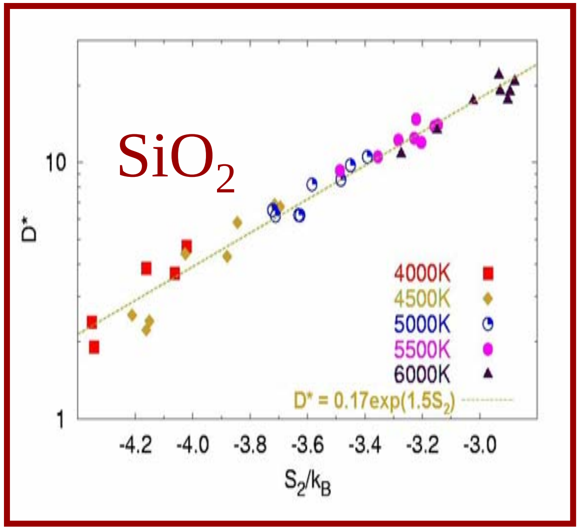




$$X^* = A\exp(\alpha S_e)$$

Provided the excess entropy of a liquid shows a well-defined minimum followed by a maximum, the system will have regime of <u>anomalous diffusional behaviour</u>



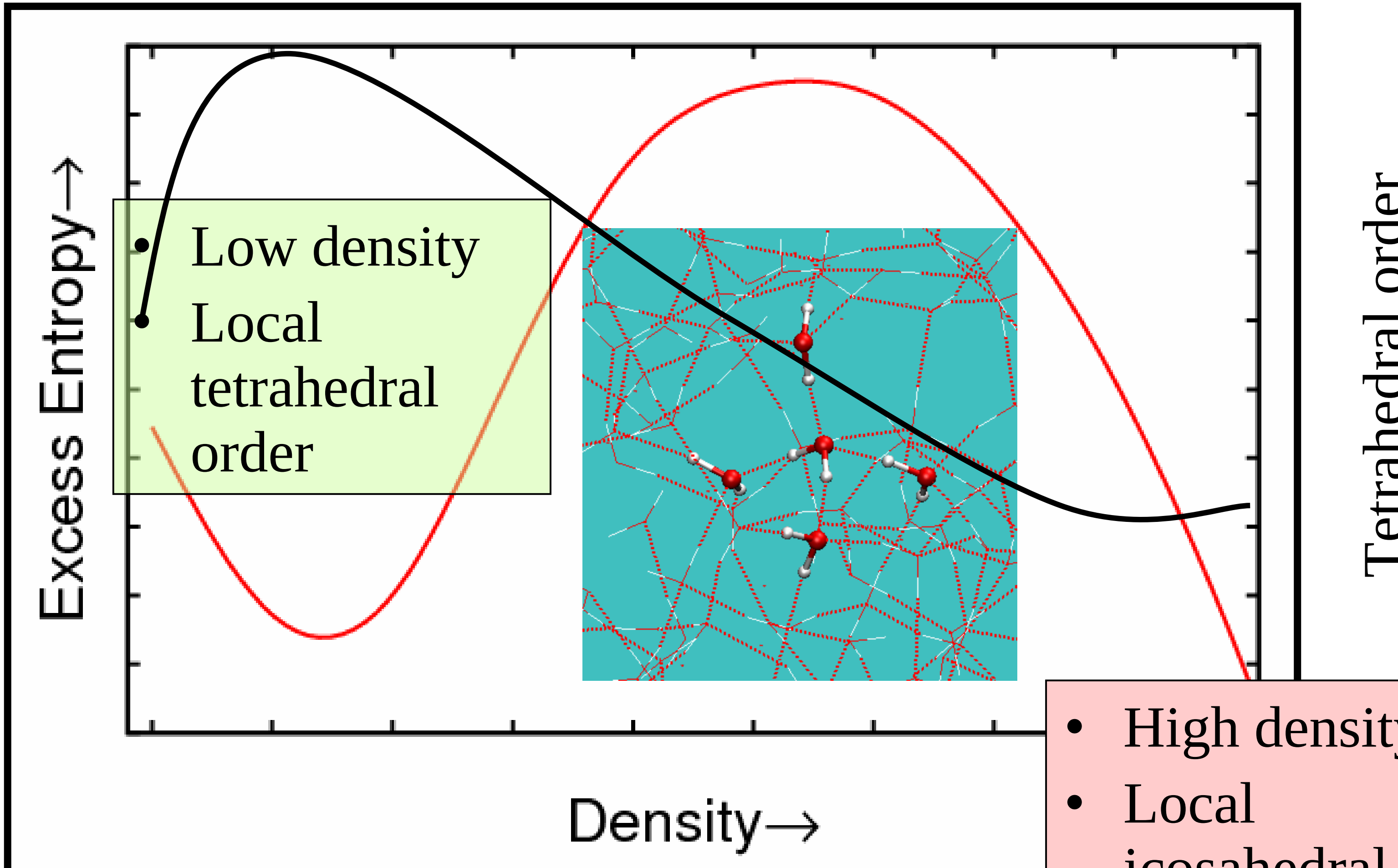


Sharma, J. Chem. Phys. (2006)

Mittal, J. Chem. Phys. (2006)

Origin of Excess Entropy Anomaly in Tetrahedral Liquids:

Change in Symmetry of Local Order on Compression

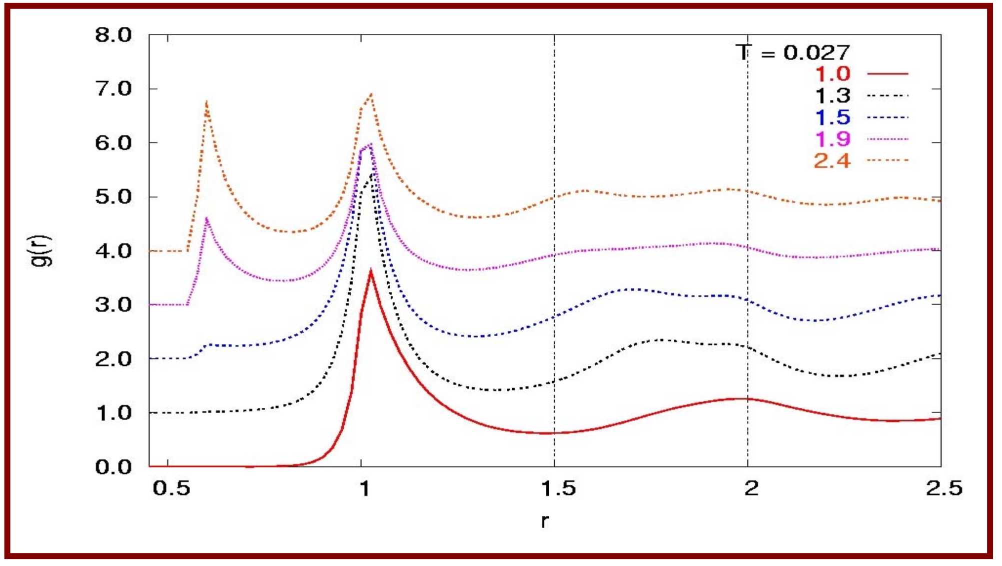


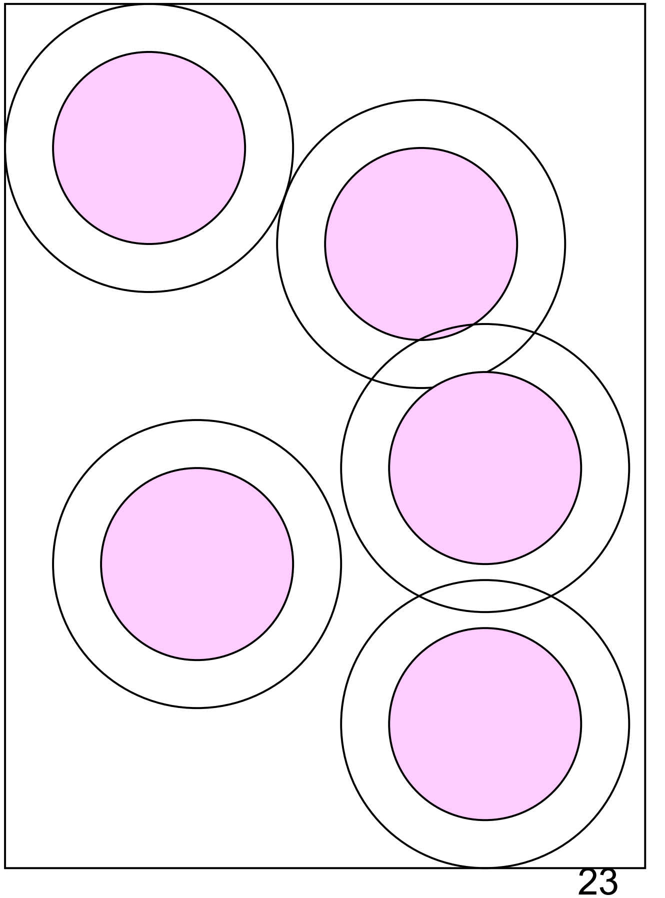
- Low density
- Local tetrahedral order

- High density
- Local icosahedral order/ simple liquid

Structural Origin of Excess Entropy Anomaly in Core-softened Fluids

Change in Length Scales on Compression



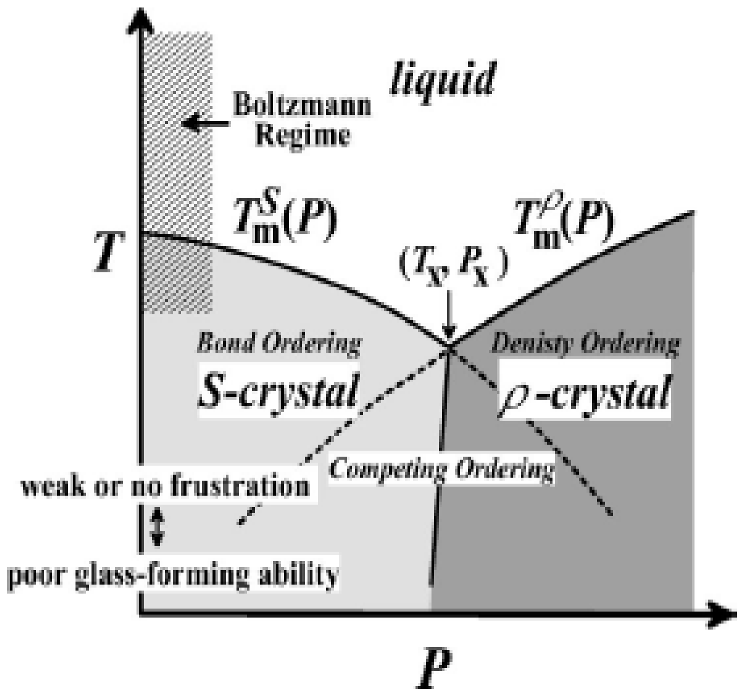


- Low density: soft-sphere diameter σ_1
  Solid has fcc structure
- High density: hard-sphere diameter σ_0
  Solid has rhombic structure
- Intermediate density: two length scales

Simple view of waterlike anomalies of atomic liquids with directional bonding

H. Tanaka,

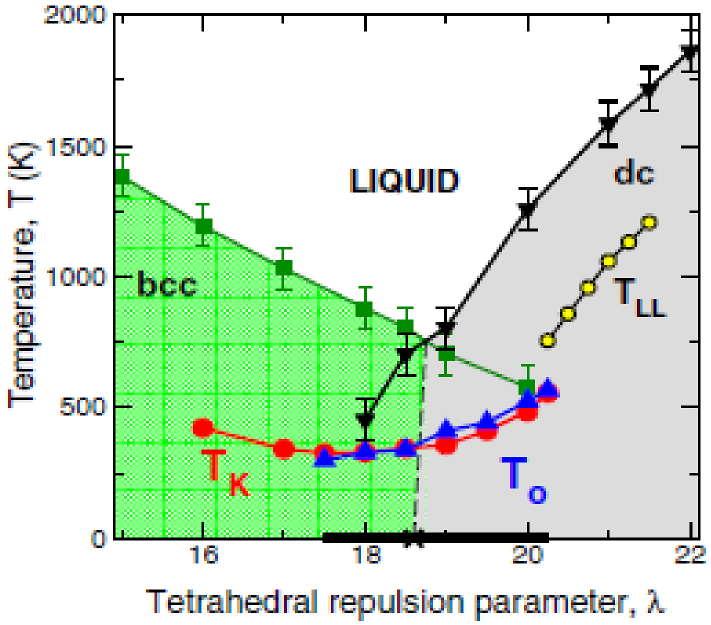
Phys. Rev. B (2002)



Tuning of tetrahedrality in modified Stillinger-Weber potential

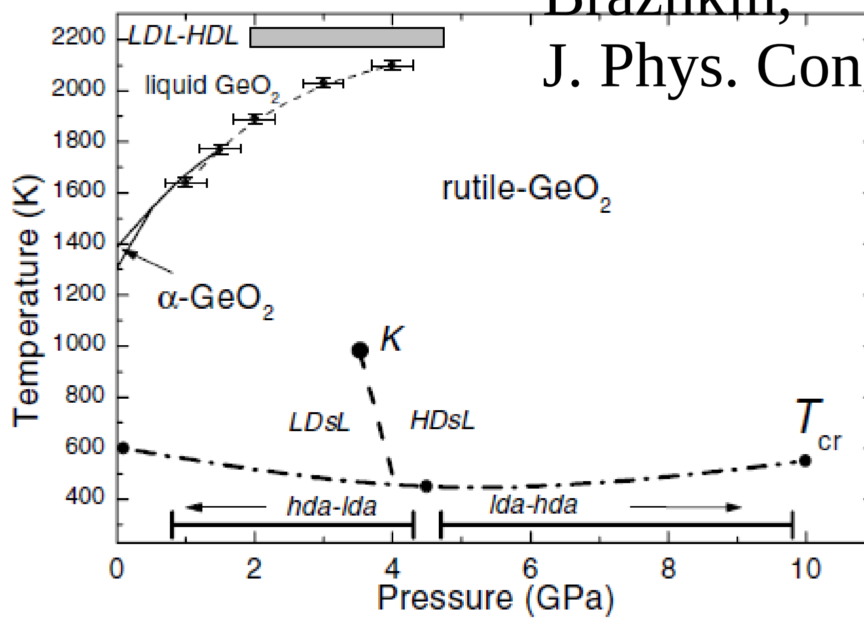
Molinero, Sastry and Angell,

Phys. Rev. Lett. (2006)

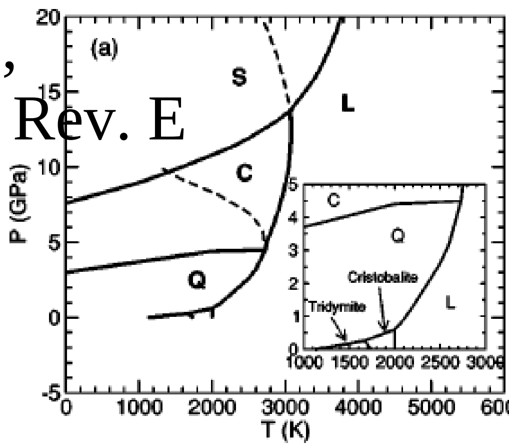


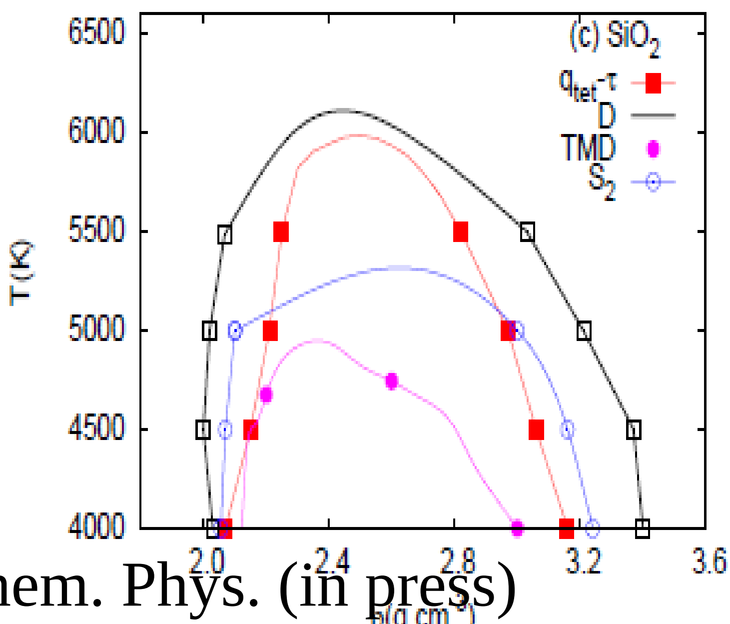
Pair Entropy Anomaly and the Phase Diagram

Brazhkin,
J. Phys. Cond. M

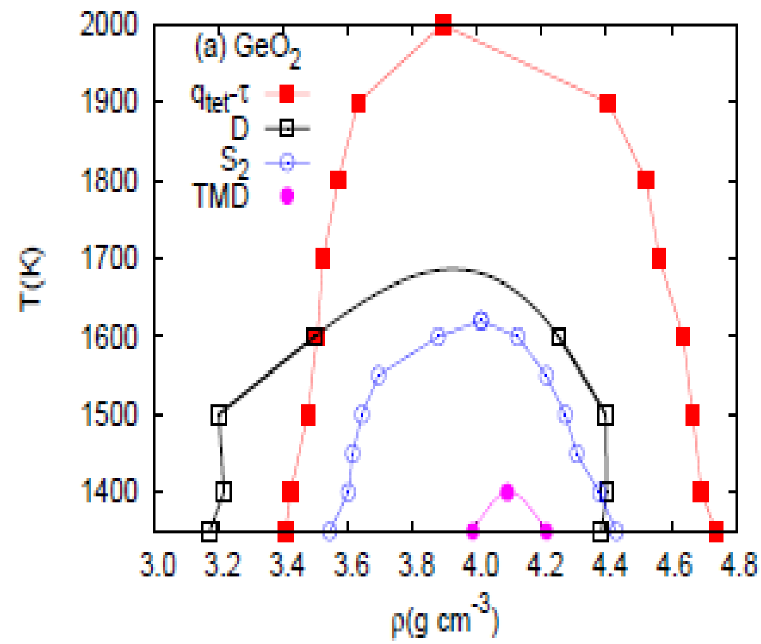


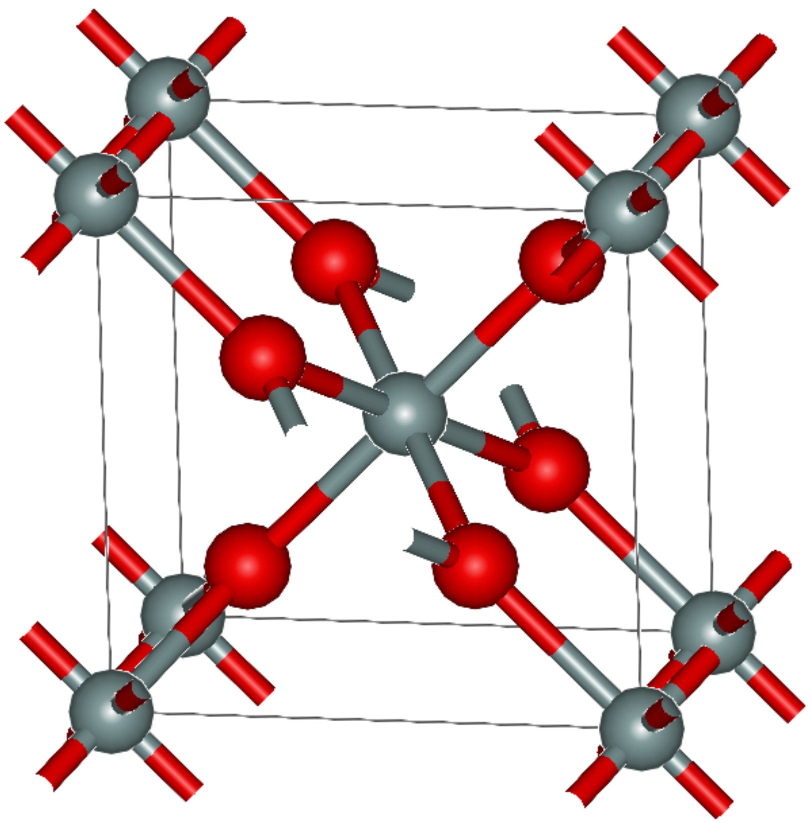
Poole,
Phys. Rev. E





J. Chem. Phys. (in press)





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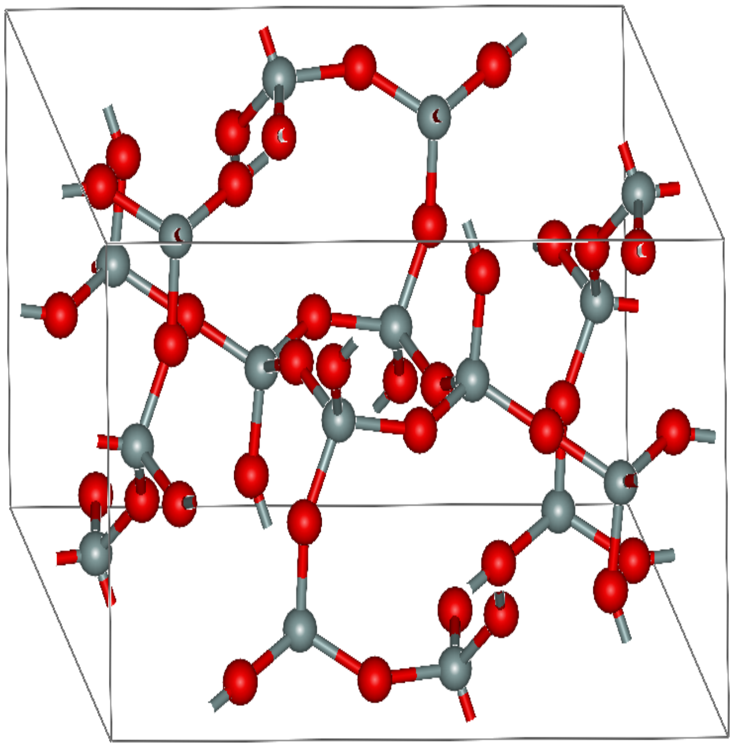

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Diffusivity, Viscosity and Ionic Conductivity

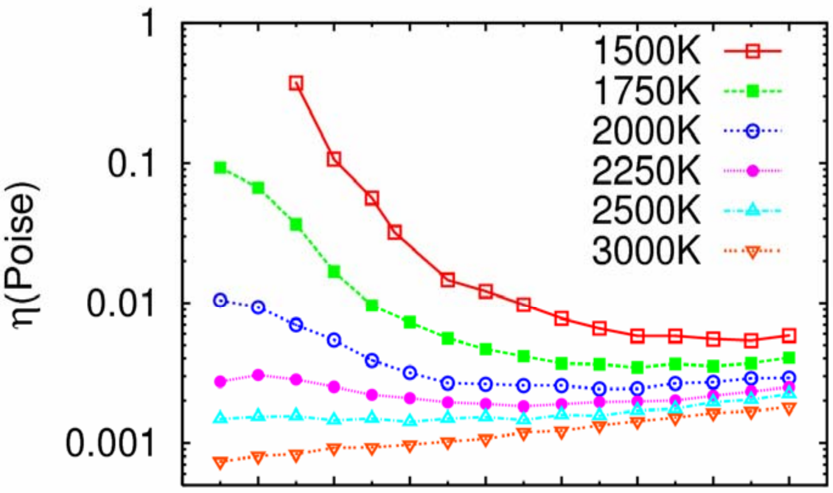
- Diffusivity: single-particle property
- Viscosity/Conductivity: collective properties
- Stokes-Einstein relation connecting diffusivity and conductivity:

$$D = k_B T / 6\pi\eta a$$

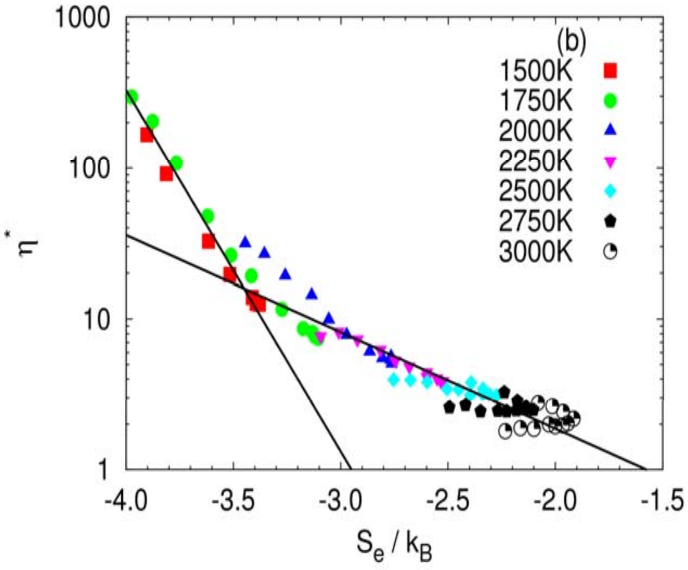
- Nernst-Einstein relation connecting ionic conductivity and diffusivity:

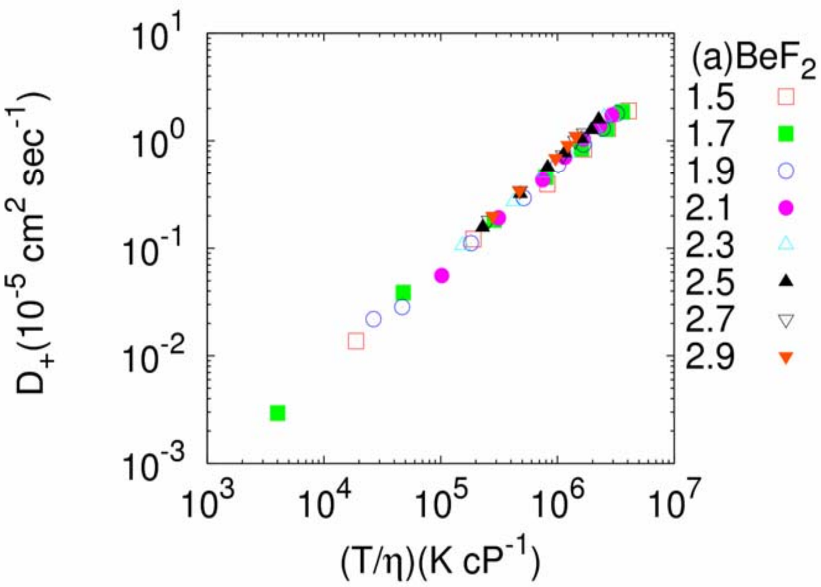
$$\sigma = \frac{e^2 \rho}{k_B T}\left(x_+ z_+^2 D_+ + x_- z_-^2 D_-\right)\left(1 - \Delta\right)$$

Stokes-Einstein Relation

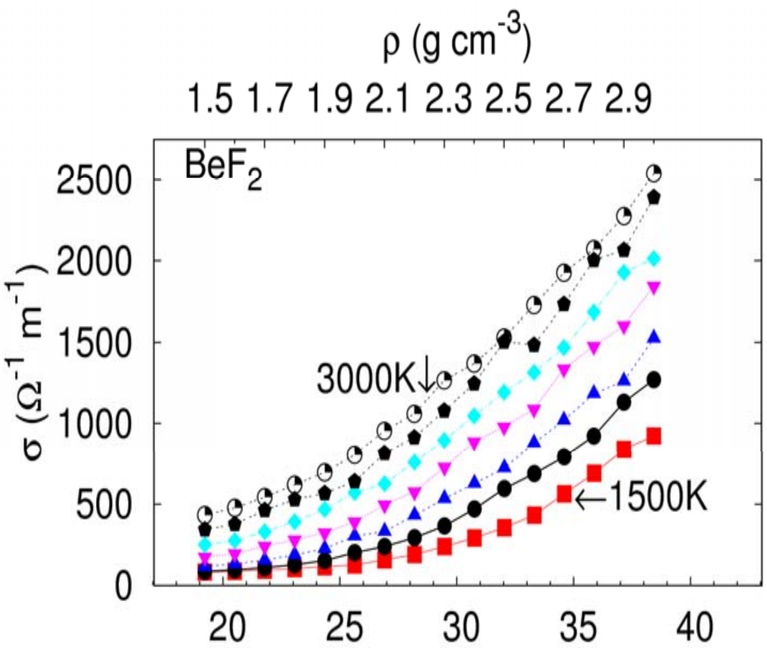


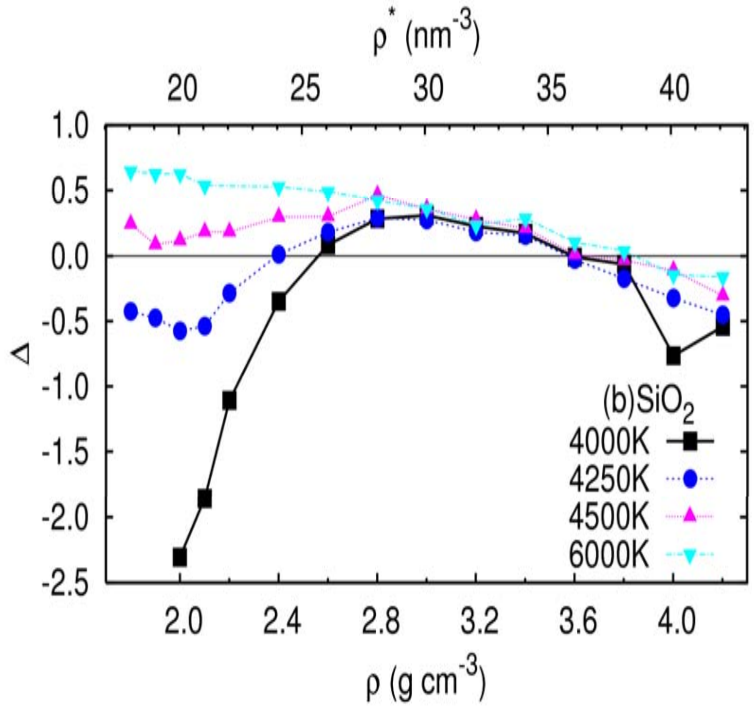
$$D = k_B T / 6\pi\eta a$$





Breakdown of Nernst-Einstein Relation





Conductivity rises monotonically over the density range associated with the diffusional anomaly.

Dramatic breakdown of the Nernst-Einstein relation in the anomalous regime

Phys. Rev. E. Rapid Comm., 2009

Excess Entropy Scaling and Water-like Anomalies

Competing types of structural order
as a function of density
May correlate with crystalline phases

↓

Structural frustration is maximum
at intermediate densities

↓

Excess/Pair Correlation Entropy Anomaly

↓

Excess entropy scaling of transport properties

↓

Mobility Anomalies

Deviations from Rosenfeld Scaling with Onset of Cooperative Dynamics

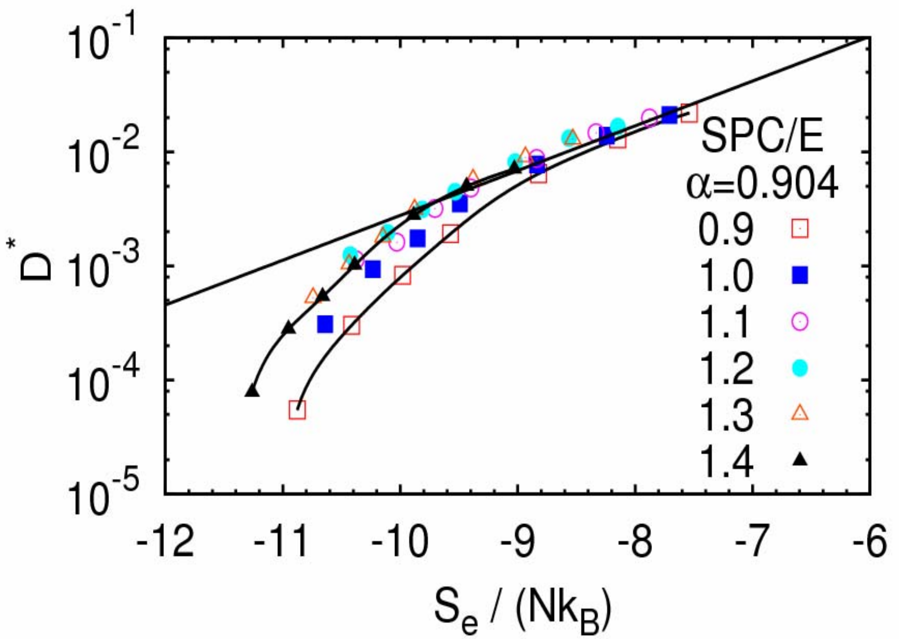
Looking more closely at Rosenfeld-scaling….

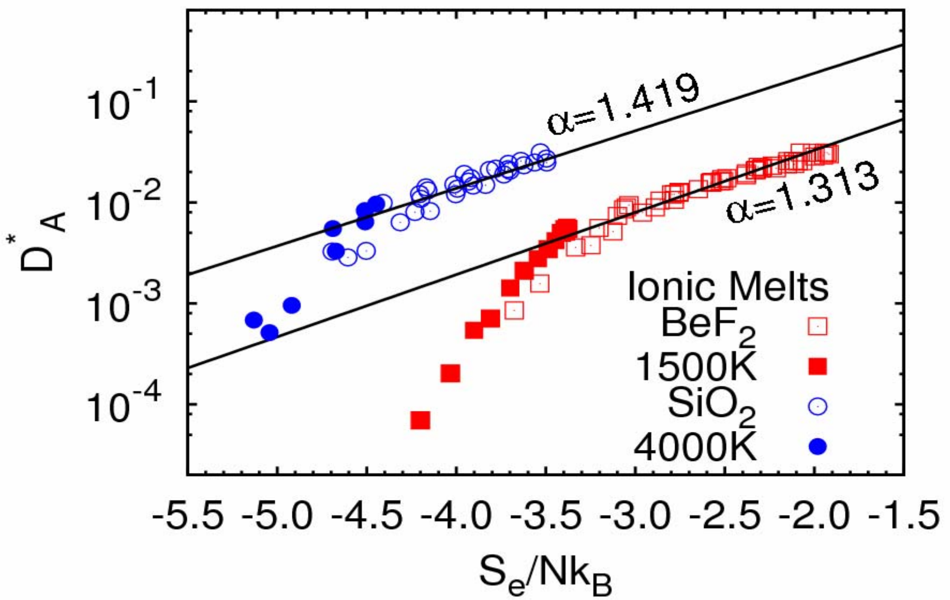
State dependence more pronounced in case of water

Onset of cooperative effects increases exponential scaling parameter

Scaling parameters system-dependent

BeF_2 SiO_2

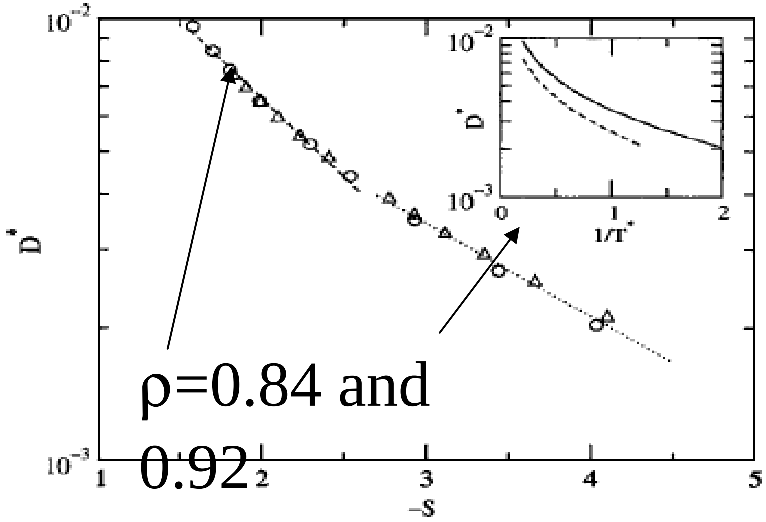




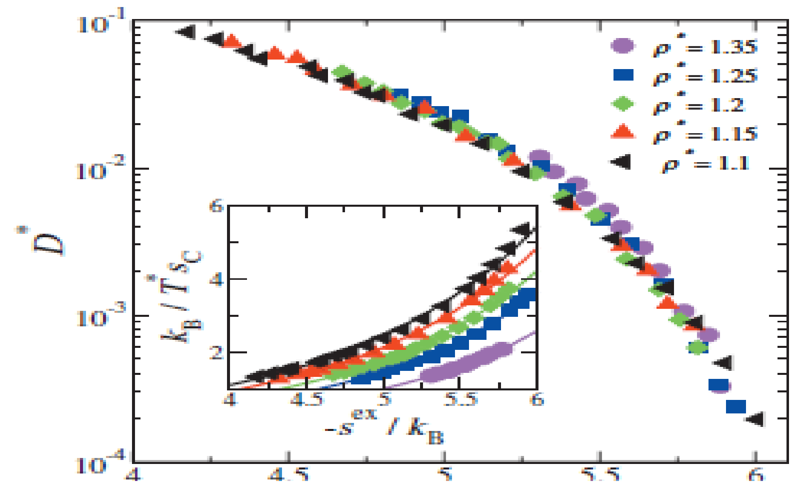
Chakravarty et al, J. Phys. Chem. (2009)

Simple Liquids and Glass-formers

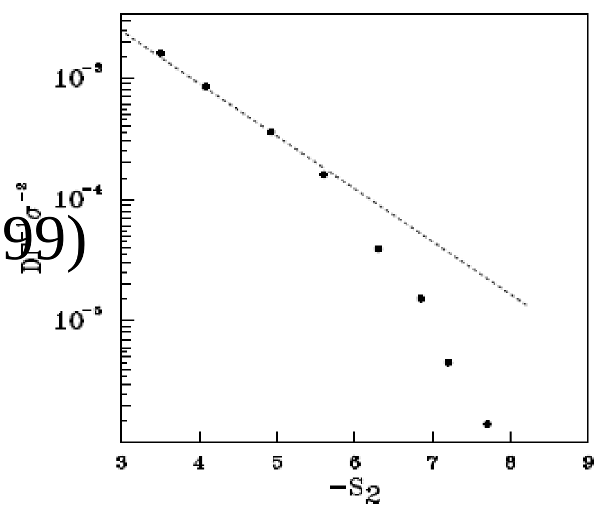
Lennard-Jones liquid,
Das et al , J. Chem. Phys., (2005)



Binary Lennard-Jones
Truskett et al, J. Chem. Phys. (2010)
Sastry, Phys. Rev. Lett. (2000)



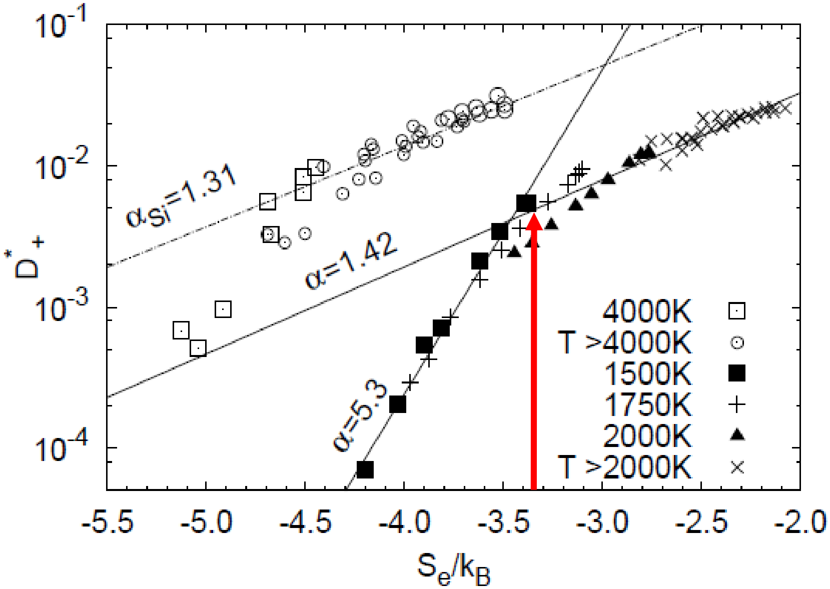
Binary hard-sphere
Dzugutov, J. Phys. Cond. Matt. (1999)

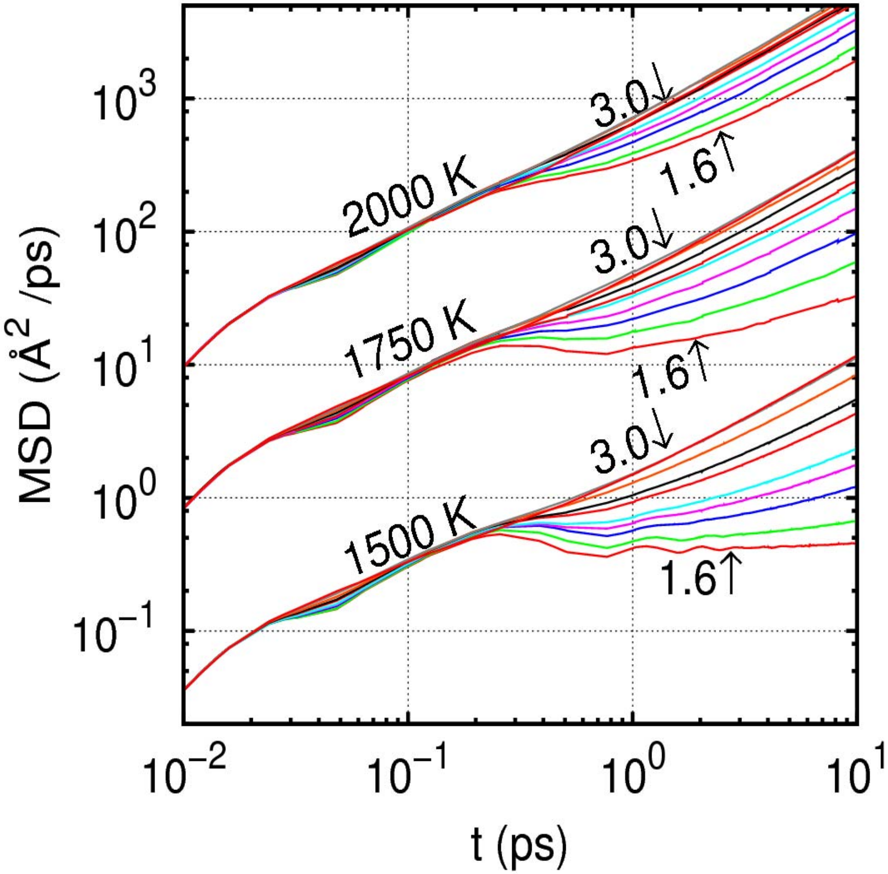


$$D^* = 0.049 \exp(S_2)$$

Deviation from Rosenfeld-scaling

Common pattern in all the systems: Fairly sharp, maybe almost discontinuous, increase in exponential scaling parameter on cooling. In BeF2, we show that this correlates with onset of local cage effects in the MSD plots.



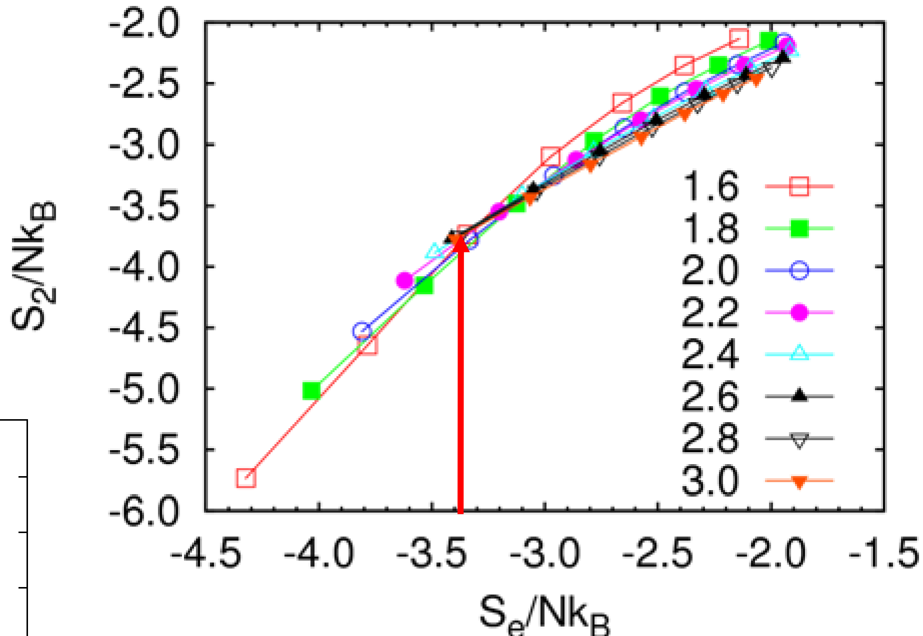


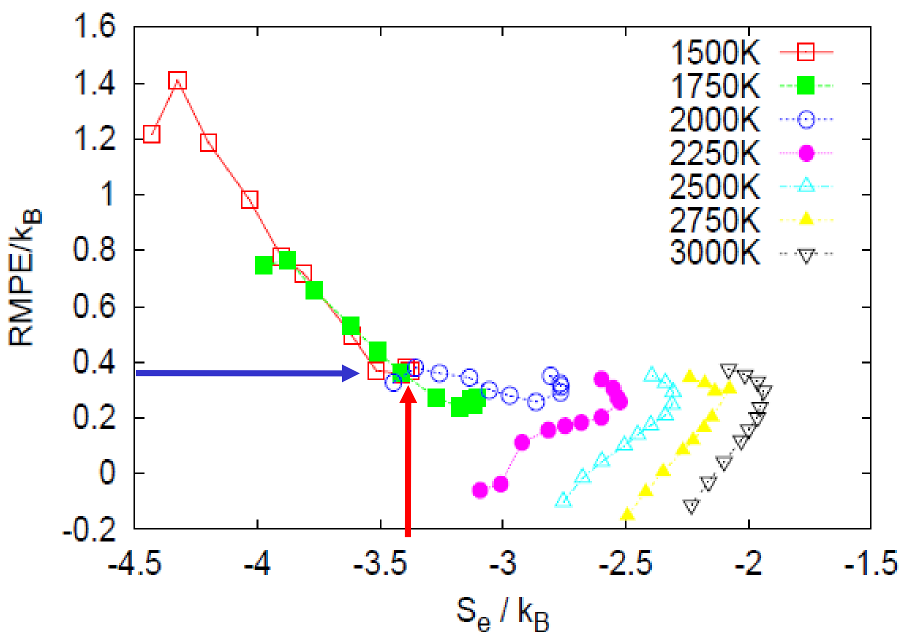
For a given isotherm, cage effect is more pronounced at lower densities

Multiparticle Correlations associated with Cage Effects

$$S = S_{id} + S_e = S_{id} + S_2 + S_3 + \ldots$$

Residual Multiparticle Entropy (RMPE): $\Delta S = S_e - S_2$



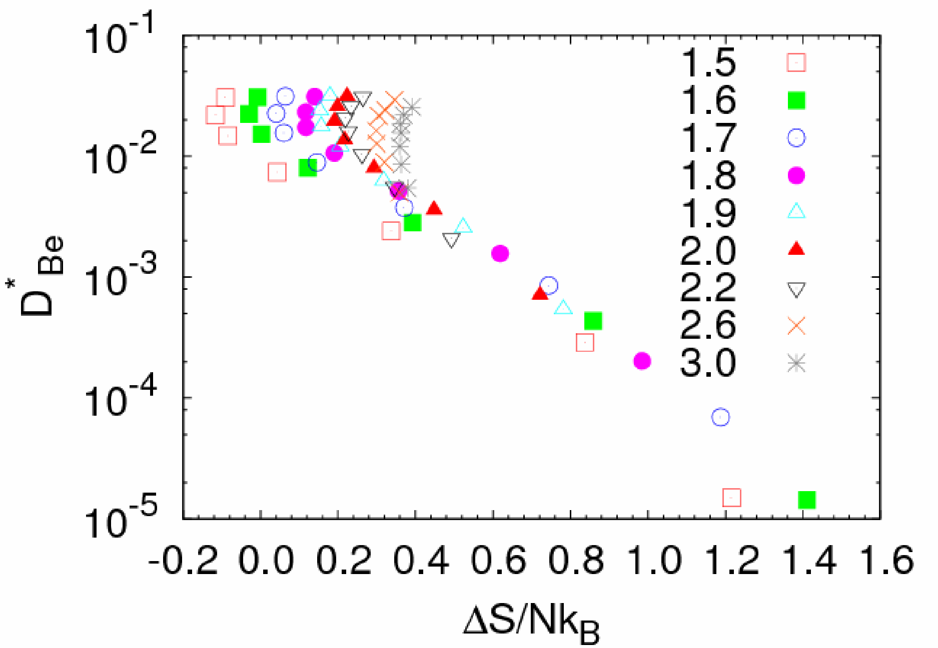


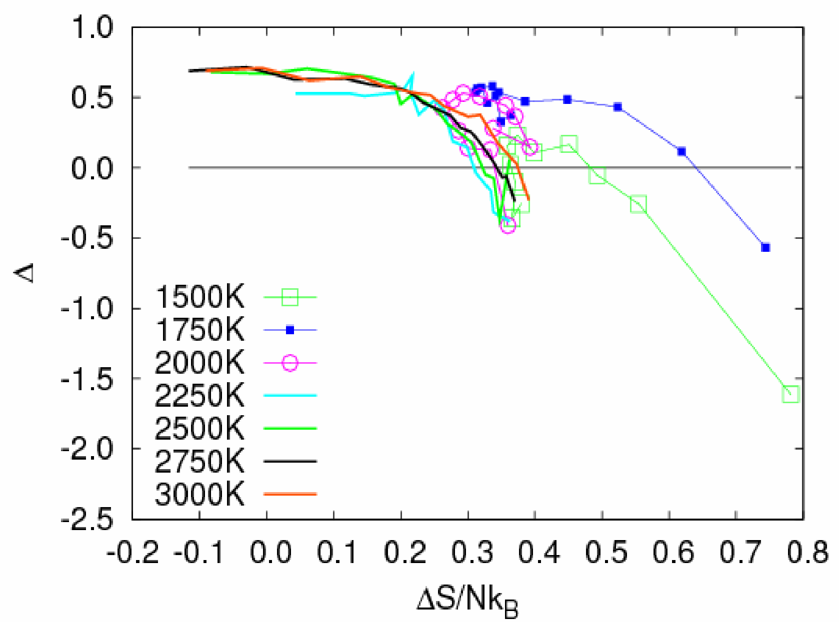
Rise in RMPE correlates witj onset of cage effects, and deviations from linear Rosenfeld-scaling.

Multiparticle Correlations and Transport Properties

Once the RMPE increases beyond 0.4kB:

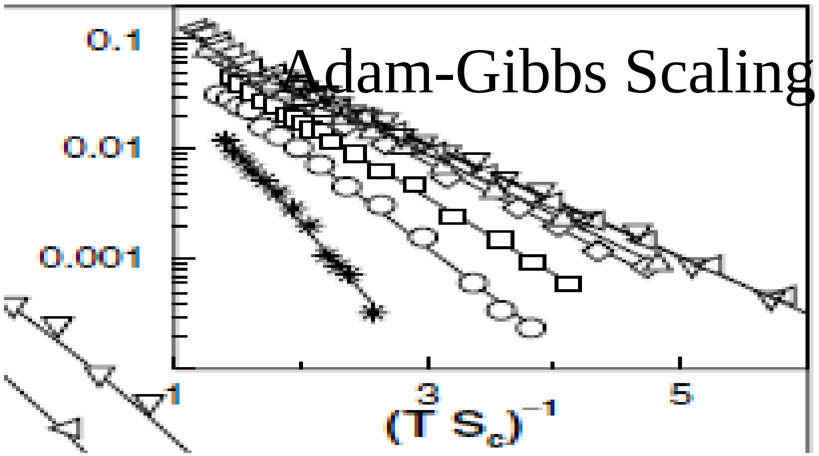
- Diffusivity is strongly correlated with RMPE
- Nernst-Einstein deviation factor becomes large and positive





Binary Lennard-Jones:

Departure from linear Rosenfeld-scaling in the landscape-influenced regime



Sastry, Phys. Rev. Lett. (2000)
Kob and Andersen, Phys. Rev. E (1995)
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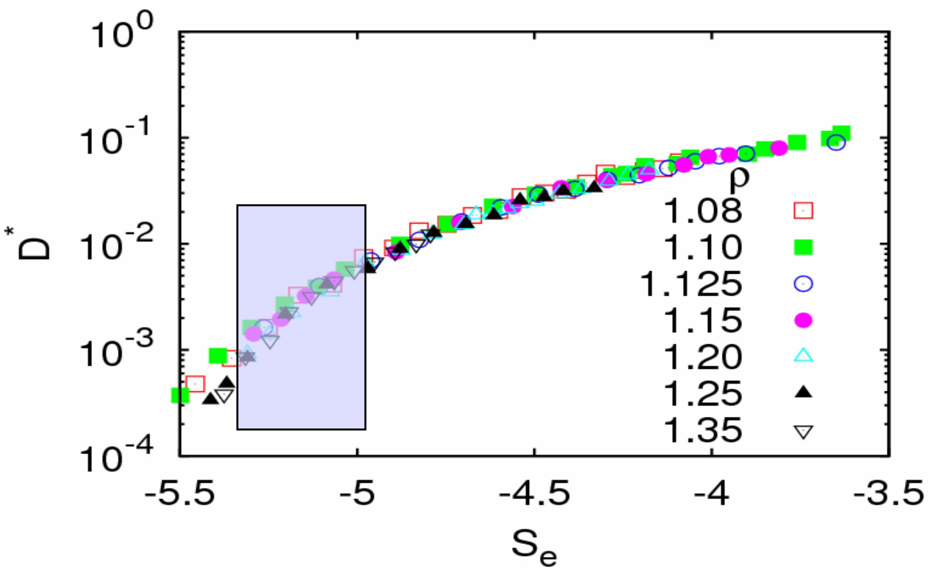
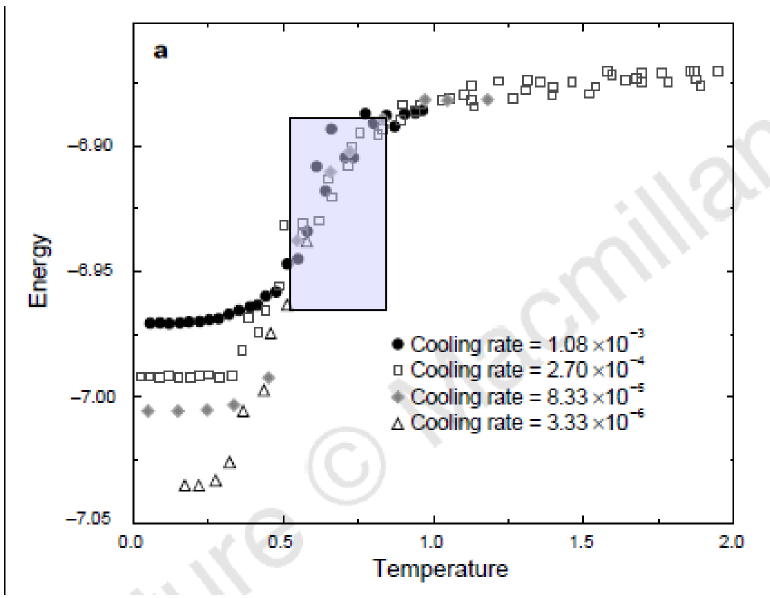
Landscape-influenced regime





Cage Effects and Excess Entropy Scaling of Transport Properties

$$\ln X^* = \ln A + \alpha S_e$$

- Onset of cage effects in time-dependent MSD is taken as signature of local, cooperative dynamics.
- Data for Rosenfeld-scaled diffusivities and the excess entropy for various state-points fall on the same curve even on supercooling for ionic melts and binary LJ. Weak isochoric dependence in water.
- The exponential scaling exponent shows a larger value at lower temperatures- transition may be very sharp.
- Rise in multiparticle correlation contributions (RMPE) correlate with:
  - Deviation from Rosenfeld-scaling
  - Local cage effect
  - Change in dynamical mechanisms of diffusivity and ionic conductivity
  - Transition of the system into a “landscape-influenced” regime.

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