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

Diffusivity

\[ X^* = A \exp(\alpha S_e) \]

Scaling parameters for simple liquids (Hoover and others)

\[ D^* = D\left(\rho^{1/3}/(k_B T / m)^{1/2}\right) = 0.6 \exp(0.8 S_e / k_B) \]

Viscosity

\[ \eta(\rho^{-2/3}/(mk_B T)^{1/2}) = 0.2 \exp(-0.8 S_e / k_B) \]

Thermal Conductivity

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


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:

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

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. \( \exp(\alpha S_e) \).

The exponential scaling parameter \( \alpha \) 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

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

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

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

[Green(1952), Baranyai (1989)]

\[ S_{id} / (Nk_B) = \frac{5}{2} - \ln(\rho \Lambda^3) \]

\[ S_2 / (Nk_B) = -2\pi \rho \int [g(r) \ln g(r) - g(r) + 1] r^2 dr \]
Pair Correlation Entropy: A convenient structural estimator of the thermodynamic excess entropy

Pair approximation to entropy of a mixture of atomic species $\alpha$ and $\beta$ with mole fractions $\chi_\alpha$ and $\chi_\beta$ can be written in terms of atom-atom radial distribution functions

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

- 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$_2$O (SPC/E)  
Ionic melt: BeF$_2$ (TRIM)

Lennard-Jones Chain fluids

Chakavarty et al  
Water
Thermodynamic and Kinetic Anomalies of Water

- Compressibility Anomaly
- Heat Capacity Anomaly
- Density Anomaly
- Diffusional Anomaly
**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.

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 \(m\).

\[
\tau = \frac{1}{\xi_c} \int_0^{\xi_c} |g(\xi) - 1| d\xi,
\]

(Debenedetti, Torquato)

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

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

(Chau & Hardwick)
Nested Structure of Anomalous Regions

Errington and Debenedetti, Nature (2001)

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

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

**Thermodynamic anomaly**: Region where $(d\rho/dT)_P > 0$.
Liquids with Water-like Anomalies
AB₂ 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.

<table>
<thead>
<tr>
<th>AB₂</th>
<th>Angle ABA</th>
<th>Tₘ(K)</th>
<th>r⁺/r⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>≅173°</td>
<td>273</td>
<td>-</td>
</tr>
<tr>
<td>BeF₂</td>
<td>≅150°</td>
<td>813</td>
<td>0.32</td>
</tr>
<tr>
<td>SiO₂</td>
<td>≅150°</td>
<td>1996</td>
<td>0.37</td>
</tr>
<tr>
<td>GeO₂</td>
<td>≅ 130°</td>
<td>1389</td>
<td>0.43</td>
</tr>
</tbody>
</table>


0.225 < Tet. Co. < 0.414
Liquids with Waterlike Anomalies: Mesoscopic Fluids with Core-softened Interactions

- Capped nanoparticles
- Star Polymers
- Colloid-polymer mixtures


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

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

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

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

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.

2-scale ramp
Sharma, Chakraborty & Chakravarty
(2006)
Excess/Pair Entropy Anomaly in molten Silica

\[ S_e \quad S_2 \]
Excess/Pair Entropy Anomaly in the SPC/E Model of Water
Excess Entropy Scaling of Diffusivities

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

\[ X^* = A \exp(\alpha S_e) \]

Origin of Excess Entropy Anomaly in Tetrahedral Liquids: Change in Symmetry of Local Order on Compression
Structural Origin of Excess Entropy Anomaly in Core-softened Fluids
Change in Length Scales on Compression

- Low density: soft-sphere diameter $\sigma_1$
  Solid has fcc structure
- High density: hard-sphere diameter $\sigma_0$
  Solid has rhombic structure
- Intermediate density: two length scales
Simple view of waterlike anomalies of atomic liquids with directional bonding
H. Tanaka,

Tuning of tetrahedrality in modified Stillinger-Weber potential
Molinero, Sastry and Angell,
Pair Entropy Anomaly and the Phase Diagram

Poole, Phys. Rev. E

Diffusivity, Viscosity and Ionic Conductivity

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

\[
D = \frac{k_B T}{6\pi \eta a}
\]

- **Nernst-Einstein relation** connecting ionic conductivity and diffusivity:

\[
\sigma = \frac{e^2 \rho}{k_B T} \left( x_+ z_+^2 D_+ + x_- z_-^2 D_- \right) (1 - \Delta)
\]
Stokes-Einstein Relation

\[ D = \frac{k_B T}{6\pi \eta a} \]
Conductivity rises monotonically over the density range associated with the diffusional anomaly.

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

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

BeF₂, SiO₂

Simple Liquids and Glass-formers

Lennard-Jones liquid,

\[ \rho = 0.84 \text{ and } 0.92 \]

Binary Lennard-Jones

Binary hard-sphere

\[ D^* = 0.049 \exp(S_2) \]
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 with 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

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.
ACKNOWLEDGEMENTS

Ph. D. students:
• Sudeshna Kar (2001)
• Pooja Shah (2003)
• Somendra N Chakraborty (2007)
• Anirban Mudi (2006)
• Ruchi Sharma (2010)
• Manish Agarwal
• Shadrack Jabes
• Murari Singh
• Divya Nayar

M.Sc. Students
• Abir Ganguly
• Mohammad Parvez Alam

Collaborators:
• Alan Oliveira
• Evy Salcedo Torres
• Marcia Barbosa
• Sanat K. Kumar
• Ram Ramaswamy
• Edoardo Milotti
• Ruth Lynden-Bell
• David Ceperley
• Pablo Debenedetti
• Frank Stillinger

Funding
Department of Science and Technology, New Delhi
Council for Scientific and Industrial Research, New Delhi
Indian National Science Academy