Supercritical fluids: Investigation of local density inhomogeneities and related properties using computer simulations.

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What is a supercritical (SC) fluid?

**P - T Phase Diagrams**

**Kτ < Kτ (ideal)**

Kτ = -1/V (∂V/∂P)T
Phase Diagram

Critical Point

\[
\frac{\partial P}{\partial V}_{T=T_c} = 0 \\
\frac{\partial T}{\partial V}_{P=P_c} = 0 \\
\frac{\partial^2 P}{\partial V^2}_{T=T_c} = 0
\]

Isothermal Compressibility

\[
\lim_{T,V \to T_c,V_c} \left[ -\frac{1}{V} \frac{\partial V}{\partial P} \right] = \infty
\]

Thermal Expansion

\[
\lim_{T,V \to T_c,V_c} \left[ \frac{1}{V} \frac{\partial V}{\partial T} \right] = \infty
\]
SF₆: Going from vapor liquid equilibrium to supercritical state and back!!
Characteristic Properties of SC Fluids

Close to the critical point:

- **VERY SMALL** pressure changes cause **VERY LARGE** changes in density and dielectric constant

  consequences

- Tuning of dissolving capability of SC solvents by adjusting the pressure

- Significant increase of the chemical reaction rates in SC solvents

Transport properties of SC fluids in comparison with liquids:

- **Self Diffusion**: 1 order of magnitude higher than in the liquid state

- **Viscosity**: 1 order of magnitude lower than in the liquid state
Applications of SC fluids

Industrial Toxic Waste Treatment

Separation Processes: Supercritical Chromatography
Fragmentation of macromolecules

Material Science: Synthesis of fine metal particles
Synthesis of nanoparticles
Synthesis of porous materials

Green Chemistry
NO hazardous waste streams,
NO harsh organic chemicals
Recyclable solvents

See:
Characteristic Local Microstructure in SC Fluids

Local Density Inhomogeneities (LDI)
Why are we interested in these Local Density Inhomogeneities?

And the answer is:

They affect significantly the properties of SC fluids

WHY?

The isothermal compressibility factor is directly related with these density fluctuations and their spatial extent (correlation length $\xi$)

Close to the Critical Point: COMPRESSIBLE REGIME
Open problems:

- Influence of thermodynamic parameters (P,V,T) on the formation of LDI

- Interrelation of these inhomogeneities with the bulk thermodynamic, structural and dynamic properties of molecular SC fluids

- Effect of intermolecular interactions on the behavior of LDI

- Dynamic behavior of LDI, Mechanisms of local environment reorganization
Theoretical Investigation of LDI

Statistical Mechanics - Molecular Simulation

How can we calculate local densities?

From the pair radial distribution function $g(r)$

$$N_c(R_c) = \rho \int_0^{R_c} 4\pi r^2 g(r) dr$$

Effective local density

$$\rho_{\text{eff,l}}(R_c, \rho) = \frac{N_c(R_c, \rho)}{N_c(R_c, \rho_{\text{ref}})} \cdot \rho_{\text{ref}}$$
Coordination number

SC Water

$\rho_{\text{ref}} \geq 2\rho_c$

Liquid-like structure


Local density augmentation (LDA)

$\Delta \rho_{\text{eff},l}(R_c, \rho) = \rho_{\text{eff},l}(R_c, \rho) - \rho$

Local density enhancement (LDE)

$F_{\text{enh}}(R_c, \rho) = \frac{\rho_{\text{eff},l}(R_c, \rho)}{\rho}$

SC Ethanol

Influence of Intermolecular Interactions on LDA and LDE

- LDE decreases with density.
- LDA maximum in range 0.6-0.8 $\rho_c$.
- LDE and LDA higher in polar, Hydrogen bonded fluids.
- Amplitudes of LDE and LDA:
  - $\text{Xe} < \text{CO}_2, \text{N}_2, \text{CH}_4 < \text{NH}_3 < \text{MeOH} < \text{H}_2\text{O}$
- No significant differences in LDE and LDA between non-dipolar systems.
- For Hydrogen Bonding fluids, Water LDE and LDA sufficiently higher than those of MeOH and NH3.

Representative Snapshots

- Methanol
- Ammonia
- Xenon
- Water
First Shell of scethanol going from low to high densities

$N_c = 2$ → $N_c = 4$

$N_c = 7$ → $N_c = 10$
Local Density Reorganization

\[ \Delta \rho_1(t) = \rho_1(t) - \langle \rho_1 \rangle \]

\[ C_{\Delta \rho_1}(t) = \frac{\langle \Delta \rho_1(0) \Delta \rho_1(t) \rangle}{\langle [\Delta \rho_1(0)]^2 \rangle} \]

\[ \tau_{\Delta \rho_1} = \int_0^\infty C_{\Delta \rho_1}(t) \cdot dt \]

Local Density Reorganization time
Length Scale Effects on the Mechanics of Local Density Reorganization

3 length scale regions with different density dependence of local reorganization times (and different time decay)

Region 1   : $r \rightarrow 0 - R_1$
Region 2   : $r \rightarrow R_1 - R_2$
First Shell: $r \rightarrow 0 - R_2$
Second Shell: $r \rightarrow 0 - R_3$
At very short intermolecular distances: 

\[ g(r) \propto \exp(-U(r)) \]

‘Direct’ Potential induced mechanism

At higher length scales: 

Collective effects start to affect the local density reorganization

As the length scale increase

The Local Density Reorganization time is maximized in the density range close to the critical density

Density Dependence of local reorganization times

Local density reorganization as a function of density and length scale

The Local Density Reorganization time is indeed maximized at higher length scales in the density range close to the critical density.

WHAT DO WE PREDICT?

Benzene

Local density reorganization processes inside the first solvation shell

\[ C_{\Delta \rho_1}(t) = C_{\Delta N_c}(t) = \frac{\langle \delta N_c(0) \cdot \delta N_c(t) \rangle}{\langle \delta N_c(0)^2 \rangle} \]

‘Direct-Pair Potential’ and ‘Collective’ contributions:

\[ N_c(R_c) = 4\pi \rho \int_0^{R_1} r^2 \cdot g(r) \cdot dr + 4\pi \rho \int_{R_1}^{R_2} r^2 \cdot g(r) \cdot dr = N_1 + N_2 \]

\[ \delta N_c(t) = N_c(t) - \langle N_c \rangle = N_1(t) + N_2(t) - \langle N_1 + N_2 \rangle = N_1(t) - \langle N_1 \rangle + N_2(t) - \langle N_1 \rangle = \delta N_1(t) + \delta N_2(t) \]

\[ C_{\Delta N_c}(t) = \frac{\langle \delta N_1(0) \cdot \delta N_1(t) \rangle}{\langle \delta N_c(0)^2 \rangle} + \frac{\langle \delta N_2(0) \cdot \delta N_2(t) \rangle}{\langle \delta N_c(0)^2 \rangle} + \frac{\langle \delta N_1(0) \cdot \delta N_2(t) \rangle}{\langle \delta N_c(0)^2 \rangle} + \frac{\langle \delta N_2(0) \cdot \delta N_1(t) \rangle}{\langle \delta N_c(0)^2 \rangle} \]

Length scale contributions on the reorganization mechanism

SC Ethanol

\[ \tau_{\Delta \rho_l} \equiv \tau_{\Delta N_C} = \int_0^\infty C_{\Delta N_C}(t) \cdot dt = \tau_{R1} + \tau_{R2} + \tau_{Cross} \]
First Solvation Shell

\[ C_{\Delta \rho_1}(t) = C_1(t) + C_2(t) = c e^{-\frac{t}{t_1}} + (1-c) e^{-\frac{t}{t_2}} \]

\[ \tau_{\Delta \rho_1} = c \cdot t_1 + (1-c) \cdot t_2 = \tau_1 + \tau_2 \]

Second Solvation Shell

The time decay is different especially at higher densities

Another indication of the change in the relaxation mechanism at larger length scales

Residence Dynamics

\[ C_{\text{res}}(t) = \sum_{i,j} \frac{\langle h_{ij}(0) \cdot h_{ij}(t) \rangle}{\langle h_{ij}(0)^2 \rangle} \]

\[ \tau_{\text{res}} = \int_{0}^{\infty} C_{\text{res}}(t) \cdot dt \]

- \( h_{ij}(t) = 1 \), if molecule \( j \) is inside the solvation shell of molecule \( i \) at times 0 and \( t \) and the molecule \( j \) has not left in the meantime the shell for a period longer than \( t^* \).

- \( h_{ij}(t) = 0 \), otherwise

- \( t^* = 0 \quad \text{Continuous} \)

- \( t^* = 2 \text{ ps} \quad \text{Intermittent-Like} \)

The residence dynamics are also different at short length scales, but not the same with local density dynamics.
Relation of HB network with LDI

Ethanol

Similar non-linear density dependence with the coordination number

Water

Higher deviation from linearity

Possible reason for higher LDA values in SC water
Relation of spectral shifts with the local density

Libration Bands in SCW

Now some experimentalists doubt previous assumptions that:

$$\omega_{\text{max}} = c \cdot \rho \ell$$

e.g. see Song, W., Maroncelli, M., Chem Phys Lett., 378, 410 (2003)

INDEED

We observe a clear non-linear behavior!

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HB Dynamics

\[ C_{HB}(t) = \sum_{i,j} \frac{\langle h_{ij}(0) \cdot h_{ij}(t) \rangle}{\langle h_{ij}(0)^2 \rangle} \]

\[ \tau_{HB} = \int_{0}^{\infty} C_{HB}(t) \cdot dt \]

- \( h_{ij}(t) = 1 \), if molecule j is hydrogen bonded with molecule i at times 0 and t and the bond has not been broken in the meantime for a period longer than \( t^* \).
- \( h_{ij}(t) = 0 \), otherwise

- \( t^* = 0 \) → Continuous
- \( t^* = \infty \) → Intermittent
Effect of mutual diffusion and reorientation on HB Dynamics

**Mutual Diffusion**

\[
C_{HB}^d(t) = \sum_{i,j} \left\langle h_{ij}(0) \cdot h_{ij}^d(t) \right\rangle_{t^*} \left\langle h_{ij}(0) \cdot h_{ij}(0) \right\rangle
\]

\[
\tau_{HB}^d = \int_0^{\infty} C_{HB}^d(t) \cdot dt
\]

- \( h_{ij}^d(t) = 1 \) if \( R_{0..0} \leq 3.5 \) Å at times \( 0 \) and \( t \) and this bond length has not been larger in the meantime for a period longer than \( t^* \).
- \( h_{ij}^d(t) = 0 \) otherwise
Mutual Reorientation

\[ C_{\text{HB}}^\phi(t) = \frac{\langle h_{\tilde{y}}(0) \cdot h_{\tilde{y}}^\phi(t) \rangle_t \cdot}{\langle h_{\tilde{y}}(0) \cdot h_{\tilde{y}}^\phi(0) \rangle} = \frac{\langle h_{\tilde{y}}(0) \cdot h_{\tilde{y}}^\phi(t) \rangle_t \cdot}{\langle h \rangle} \]

- \( h_{\tilde{y}}^\phi(t) = 1 \) if the donor-acceptor angle \( H - O \ldots O \leq 30^\circ \)
- \( h_{\tilde{y}}^\phi(t) = 0 \), otherwise

at times 0 and t and this angle has not been larger in the meantime for a period longer than t*.

Intermittent Case

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Effect of mutual diffusion - reorientation on HB Dynamics

Especially for Continuous dynamics

Mutual reorientation mechanism seems to be more important than mutual diffusion in the case of HB dynamics


Similar behavior with residence dynamics at short length scales
What about single molecule dynamics?

**Single Reorientational Dynamics**

\[ C_{lr}(t) = \langle P_l(\vec{u}(0) \cdot \vec{u}(t)) \rangle, \quad l = 1, 2. \]

Legendre Reorientational tcfs

**MeOH**


Different density dependence for reorientational modes related with stronger interactions (e.g. O-H in methanol)
SC Ethanol

Different Behavior of 1\textsuperscript{st}, 2\textsuperscript{nd} order Legendre dynamics

3 groups of vectors exhibiting similar density dependence

Plateau for 2\textsuperscript{nd} order correlation times related with weaker interactions

Effect of the H B network on single reorientational dynamics

The H B network around each molecule affects significantly its single reorientational dynamics.

Plateau for 2\textsuperscript{nd} order correlation times are observed for free (non-H B) molecules and for modes related to weak interactions.
● 1st order Legendre reorientational dynamics more affected by the local environment

● Modes related with weak interactions are not affected by LDI in the case of 2nd order Legendre reorientational dynamics
Effect of the H B network on single translational dynamics

SCW (SPC/E)

Significant influence of the H B network on single translational dynamics!

The libration band peaks are shifted towards higher $\omega$ values for more strongly H Bonded water molecules

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As the bulk density increases, the peaks shift towards higher frequencies. Plateau behavior in the case of more strongly H-Bonded molecules (e.g. $n_{\text{HB}} = 3$)
Dependence of the local HB network on the C.O.M. motion
Effect of the H B network on single O-H reorientational dynamics
Density Dependence

Further work in progress....

HB Dependence
FIN

Muchas gracias!

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