
Non-linear statistical physics and Molecular
Dynamics simulations for the interpretation
of Time-resolved X-ray diffraction

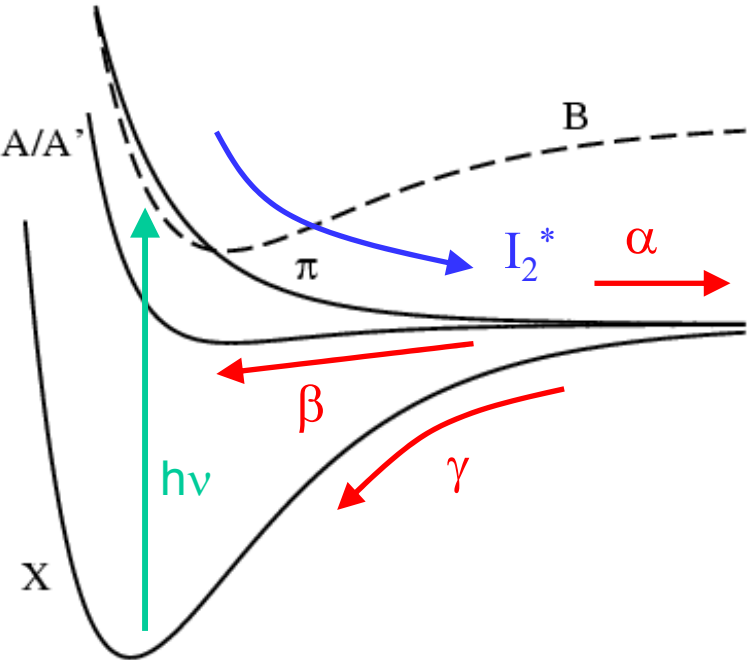
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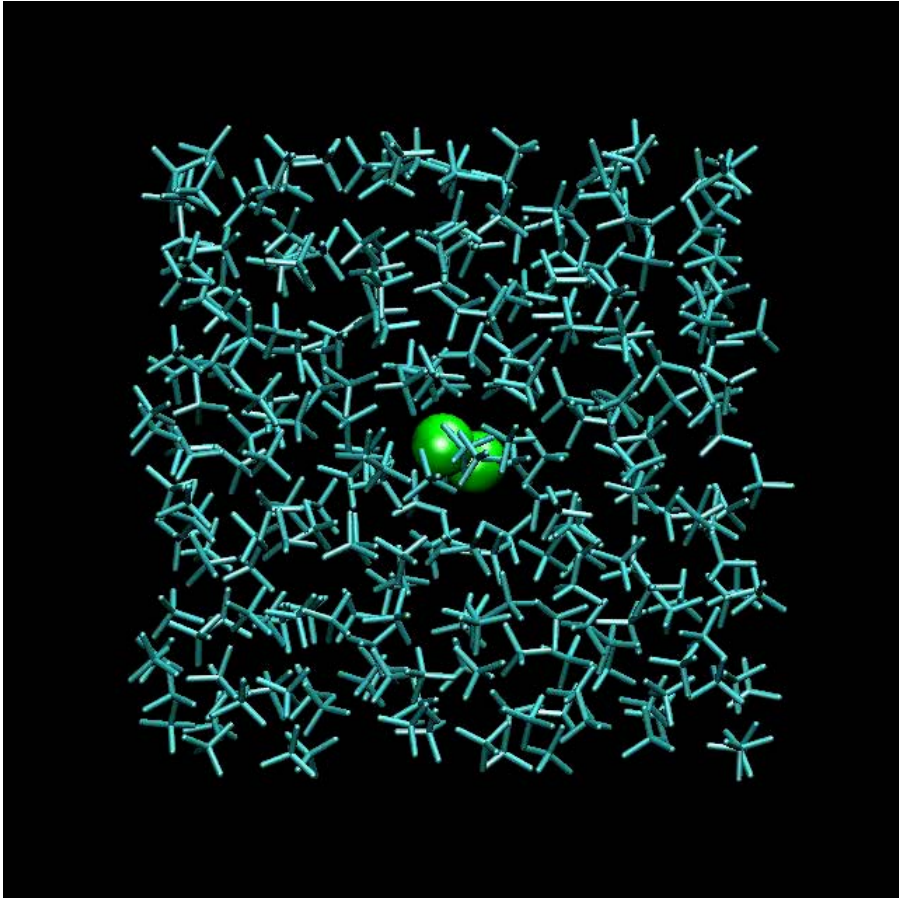
ID09, ESRF, Grenoble

Photodissociation of Iodine



α : non geminate recombinaison

β, γ : geminate recombinaison



General formula for pump-probe x-ray diffraction

$$\Delta S(\mathbf{q}, \tau) = S(\mathbf{q}, \tau) - S_0(\mathbf{q}); \quad \Delta S(\mathbf{q}, \tau) = \int_{-\infty}^{\infty} I_X(t - \tau) \Delta S_{inst}(\mathbf{q}, t) dt$$

At second order in perturbation theory:

$$\Delta S_{inst}(\mathbf{q}, t) = - \left[\frac{e^2}{m c^2 \hbar} \right]^2 P \times \int_0^{\infty} \int_0^{\infty} \langle E_i(\mathbf{r}, t - \tau_1) E_j(\mathbf{r}, t - \tau_1 - \tau_2) \rangle_0 \\ \times \langle [\tilde{s}(\mathbf{q}, \tau_1 + \tau_2), [\tilde{M}_i(\tau_2), \tilde{M}_j(0)]] \rangle_S d\tau_1 d\tau_2$$

$$\tilde{s}(\mathbf{q}, \tau) = f^2 \int 4 \pi^2 \tilde{n}(\mathbf{r}, \tau) \frac{\sin(qr)}{qr} dr$$

Separation of time scales – slow variables

At long times:

- **slow variables** are still correlated
- fast variables are assumed to be at equilibrium at fixed value of the slow variables

$$\Delta S_{inst}(q, t) \approx \mathbf{S}(t) \times \langle \Delta \tilde{s}(q) \rangle_{\mathbf{S}=\mathbf{S}(t)}$$

Identification of the slow variables:

- **concentrations** of the species: $I_2^*(A/A')$ (n_β) and $I+I$ (n_α)
- but also **hydrodynamics modes**: $T[k]$, $\rho[k]$, $P[k]$, $j[k]$ for $k > k_c$
fed by **heating** of the solvent following the chemical reactions

Model signal for I_2 in CCl_4 – phenomenological equations

- Assuming a separation of time-scales and a quasistatic limit
- β (*geminate* recombinaison) and α (*non-geminate* recombinaison) :
simple kinetic models

$$\left\{ \begin{array}{l} \Delta S_{inst}(q, t) = n_\alpha(t) \Delta S_{I_2, \alpha}(q) + n_\beta(t) \Delta S_{I_2, \beta}(q) + \Delta S_{CCl_4}(q, t) \\ \frac{\partial}{\partial t} n_\beta = -\frac{1}{\tau_\beta} n_\beta \quad (\tau_\beta = 2.7 \text{ ns}) \quad \frac{\partial}{\partial t} n_\alpha = -k_\alpha n_\alpha^2 \quad (k_\alpha = 0.72 \cdot 10^{-2} \text{ M}^{-1} \cdot \text{ps}^{-1}) \end{array} \right.$$

$\Delta S_{CCl_4}(q, t)$: change in solvent form-factor due to heating

$$\Delta S_{CCl_4}(q, t) = \left. \frac{\partial S_{CCl_4}}{\partial \rho} \right]_T \delta \rho(t) + \left. \frac{\partial S_{CCl_4}}{\partial T} \right]_\rho \delta T(t)$$

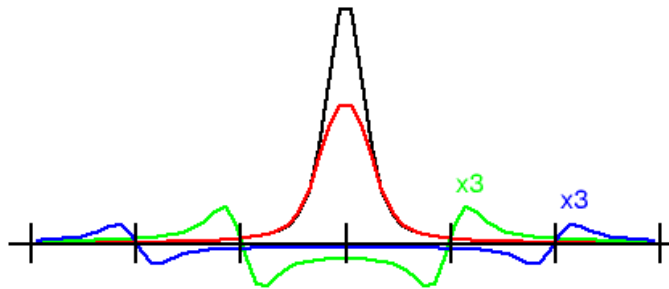
Solvent response - pressure relaxation

- The induced chemical reaction releases heat, $\delta Q(t)$, into the solvent
- Leads to an increase of temperature
- From linearized hydrodynamics equations:

$$\Delta_r \delta P - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \delta P = - \frac{\beta \rho}{C_p} \frac{\partial^2}{\partial t^2} \delta Q$$

Pressure relaxes with a time-scale of $L/c = 60$ ns (Acoustic horizon)

Propagation of a pressure front:



Validity of hydrodynamics

- Hydrodynamics probably valid for length scales of about 10 molecular radius
- $k_c^{-1} \approx 40 \text{ \AA}$, while variations of density and temperature is over length scales of 50 to 100 μm
- However modes at 40 \AA relax in about 100-200 ps (thermal diffusion)
- Other modes also relax in about 100 ps (vibrational relaxation)

delay times larger than 100 ps

Liquid structure factors

- The structure is described by the partial radial distribution functions
- One pure iodine term: $g_{I-I}(r)$
- Three solvent terms: C-C, Cl-Cl and C-Cl
- Two mixed terms: I-C and I-Cl (cage effects)

Molecular Dynamics simulations

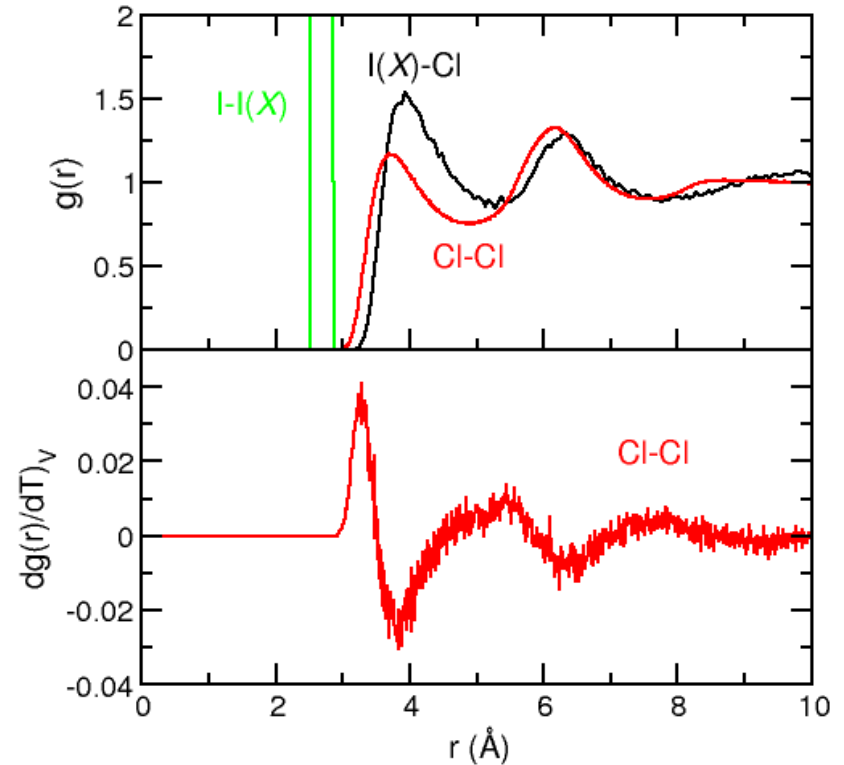
Solvent:

- rigid molecules (tetrahedrons)
- **point charges** and **Lennard-Jones** potentials (OPLS)

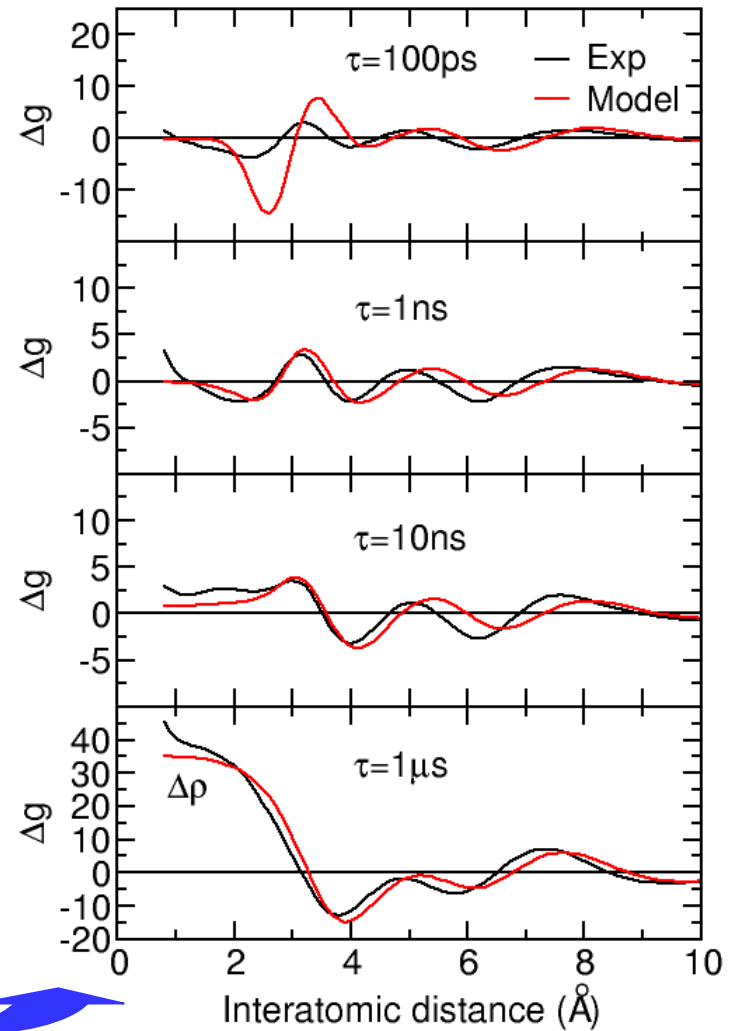
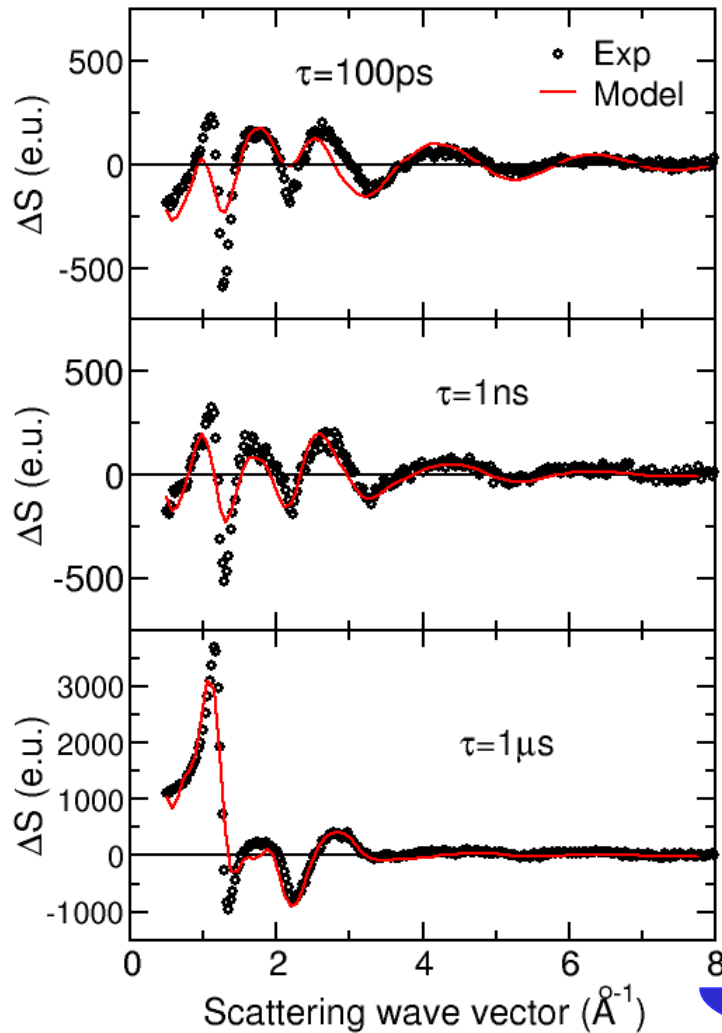
Iodine:

- flexible I_2 molecule (Morse potentials)
- **no charges**, **Lennard-Jones** potentials (same for all electronic states)

512 molecules

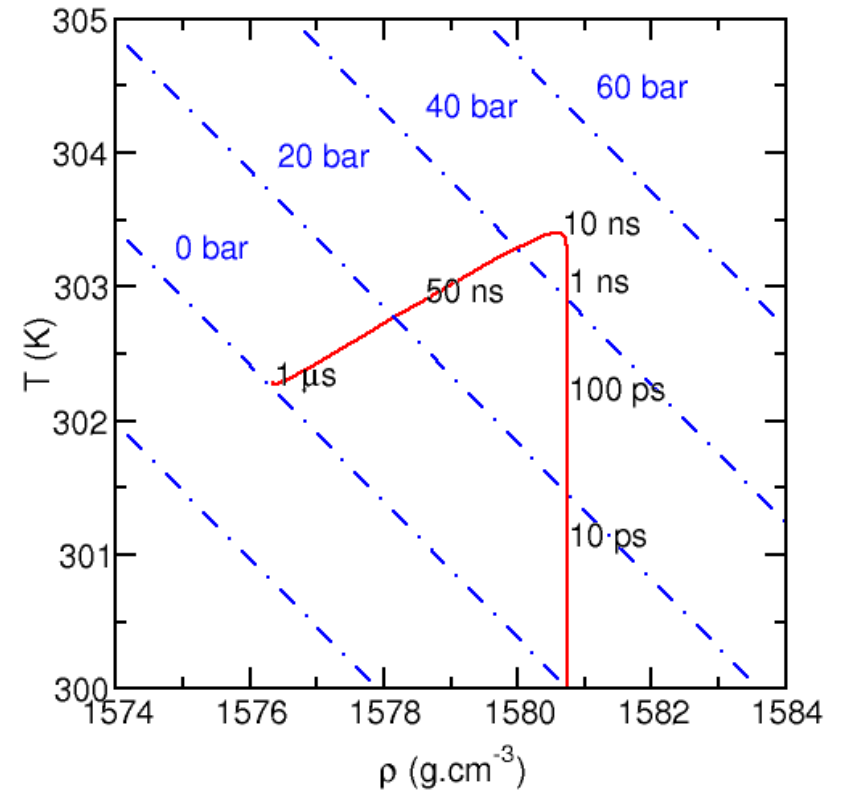
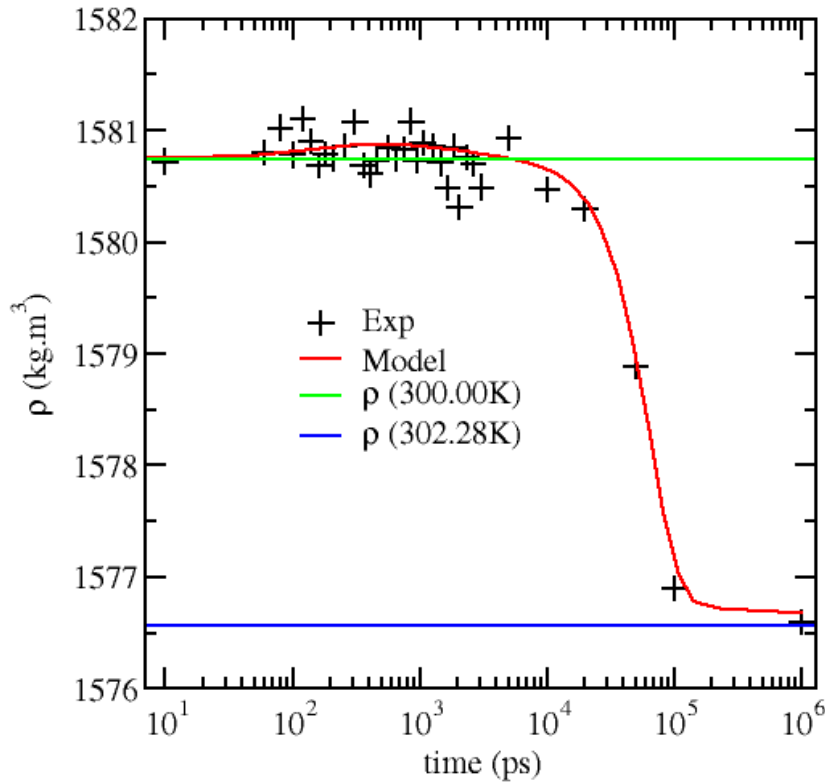


Results of least square fitting: $n_\alpha(0) = 7\%$, $n_\beta(0) = 12\%$, $n_\gamma(0) = 34\%$



$$\Delta g(r, \tau) = \frac{1}{\rho 2\pi^2 r} \int_0^\infty q \Delta S(q, \tau) \sin(qr) dq$$

Thermodynamics cycle



Conclusions

- We have reproduced the time-dependent radial distribution functions $\Delta g(r, \tau)$
- Determination of the thermodynamical cycle of the solvent
- What happens at very fast time scales when hydrodynamics does not apply? (towards tracking the solvent motion during solvation or energy redistribution?)
- More complex systems