Simulation of dissociation and caging inside helium clusters
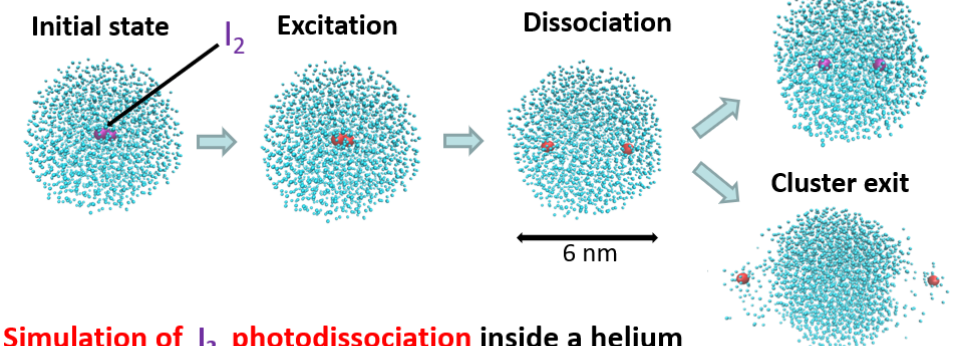
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The dissociation dynamics of molecules embedded in a condensed matter matrix is theoretically and experimentally well studied for macroscopic situations. Generally, excitation above a molecular fragmentation limit can lead to two scenarios depending on the details of the energy dissipation dynamics. The first one is fast recombination (the cage effect, see for example [1]) and the second the long time survival of separated fragments. In a cluster environment a third scenario becomes possible, namely fragments leaving the cluster with or without attached cluster particles. Helium clusters are a very cold (about 0.5 K) but still liquid and dense environment with particularly challenging properties due to the pronounced collective quantum behavior of helium leading to unusual energy dissipation dynamics. We present first results of simulations of the photodissociation of molecular iodine, I_2, at various excitation energies inside helium clusters with several thousand atoms using a technique based on quantum effective potentials [2] to account for the quantum effects. We obtain cluster size dependent threshold energies for caging, velocity distributions of photofragments exiting from the clusters and statistics about the number of helium solvent atoms carried along by the iodine atoms similar to experimental results obtained for CH_3I [3].

The photodissociation of molecular iodine has been intensely studied in the gas phase and in gas mixtures [1,4]. Vertical electronic excitation of I_2 in its X $^1\Sigma_g^+$ ground state at moderate energies leads into the continuum of the weakly bound A state and allows direct dissociation into atoms [5]. The uninhibited separation of the two iodine atoms in the gas phase is modified by the presence of collision partners in dense gases or liquids which will drain energy from the photofragments such that recombination can become favored. Photofragments may leave a cluster environment at significant residual energies with a velocity distribution which carries information about the multiple collision dynamics.

We model the photodissociation of iodine molecules at a given excitation energy by adding the equivalent amount of kinetic energy to the two iodine atoms. The compound system of two iodine atoms inside a large helium cluster equilibrated at an energy corresponding to 0.4-0.5 K then evolves microcanonically in time on a many body potential which is modelled as a sum of an I-I X state interaction and I-He and quantum effective He-He interactions. The key assumption of this model is very fast relaxation from the A state continuum into the X state continuum [1]. The trajectories are then analyzed to extract velocity and fragment size distributions.

Reactivity in a very cold, dense and liquid environment providing energy dissipation

Caging and slow recombination

Initial state — I_2 — **Excitation** — **Dissociation** — **Cluster exit**

6 nm

Simulation of I_2 photodissociation inside a helium nanodroplet (quantum liquid nano-laboratory at 0.5 K)

Method: Quantum effective potential + ZPAD

Helium delocalisation at low temperature
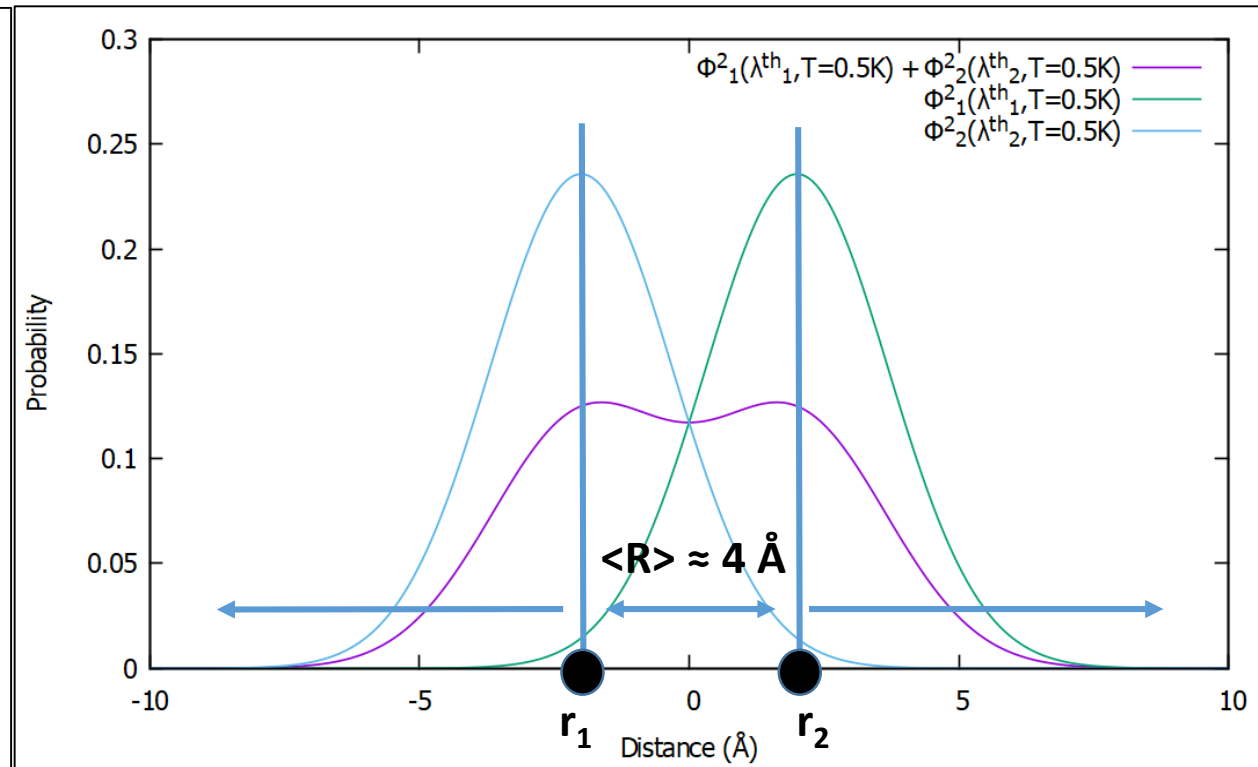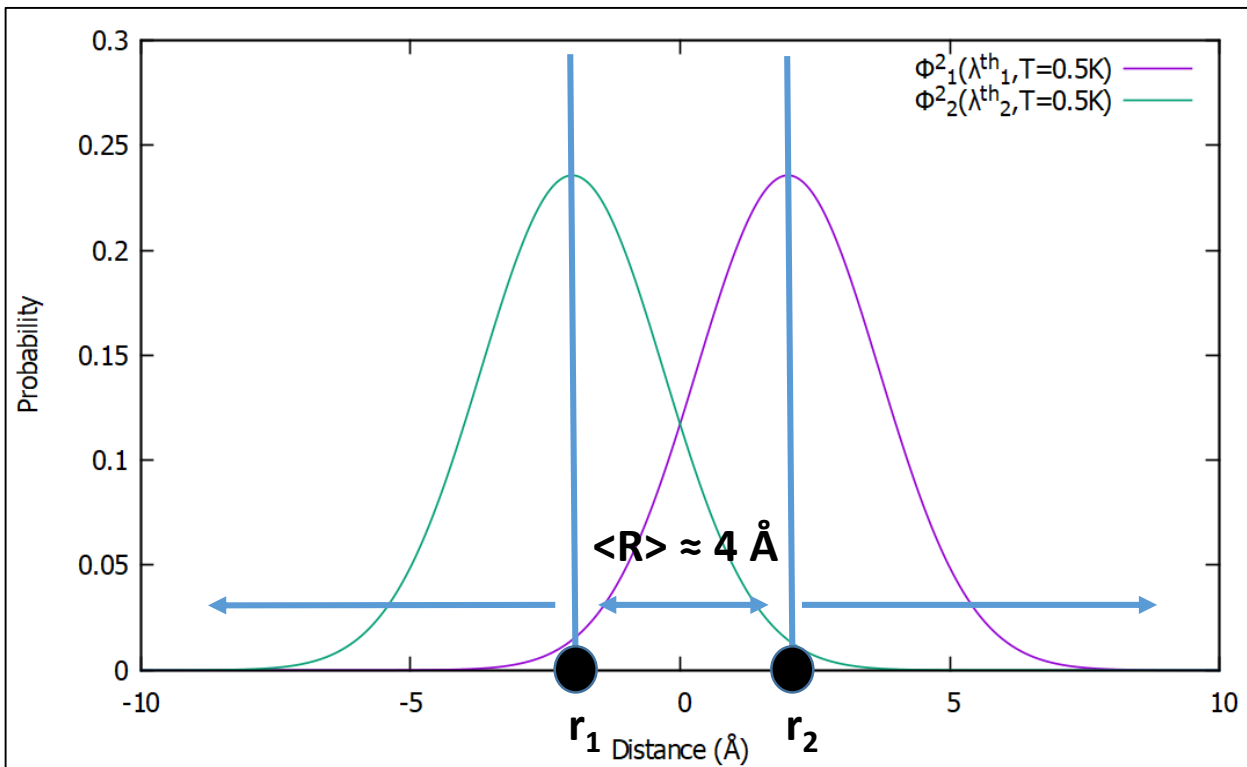
Thermal de Broglie wavelength

$$\lambda_{th}^{q} = \frac{h}{\sqrt{2\pi m k_B T}} = \hbar\sqrt{\frac{2\pi}{m k_B T}}$$

$$\lambda_{th}^{q} \approx 6\ \text{Å at } T = 0.5\ \text{K}$$

• Potentials

 - He ⋯ He: **effective potential** taking the **ZPE** into account on average
   (Portwich 1995, Slavíček et al., JPCA 2003; Sterling et al., JCP 1995)

$$V_{eff}(\underline{R}) = \iint V(\underline{R}+\underline{r}_1-\underline{r}_2)\ \Phi_1^2(\underline{r}_1)\ \Phi_2^2(\underline{r}_2)\ d\underline{r}_1 d\underline{r}_2$$

Iterative construction of Φ_1 et Φ_2

# Iterative construction of the effective potential :

1. Take the potential $V_{eff}^{(n)}(\underline{R})$ $(V_{eff}^{(1)} = V^{cl})$ and run classical MD to construct a pair correlation function $P^{(n)}(\underline{r})$

2. Convolute $P^{(n)}(\underline{r})$ with the single particle quantum density $\{\Phi_j^{(n)}(\underline{r}_j)\}^2$ (n=0 → δ-function) to construct the **n-th** quantum version $P^{(q,n)}(\underline{r})$

3. Construct a single particle radial potential $V_s(\underline{r})$ according to $V_s^{(n)}(\underline{r}_j) = \int V^{cl}(\underline{r}_j-\underline{r}) \, P^{(q,n)}(\underline{r}) \, d\underline{r}$

4. Solve the radial Schrödinger equation in $V_s^{(n)}(r_j)$ to obtain $\Phi_j^{(n+1)}(\underline{r}_j)$

5. Convolute the classical potential with the current wave functions to obtain the (n+1)-th effective potential: $V_{eff}^{(n+1)}(\underline{R}) = \iint V^{cl}(\underline{R}-\underline{r}_1+\underline{r}_2) \{\Phi_1^{(n+1)}(\underline{r}_1)\}^2\{\Phi_2^{(n+1)}(\underline{r}_2)\}^2 \, d\underline{r}_1 d\underline{r}_2$

6. Compare with previous iteration and stop if $V_{eff}^{(n+1)} \approx V_{eff}^{(n)}$, otherwise back to step 1
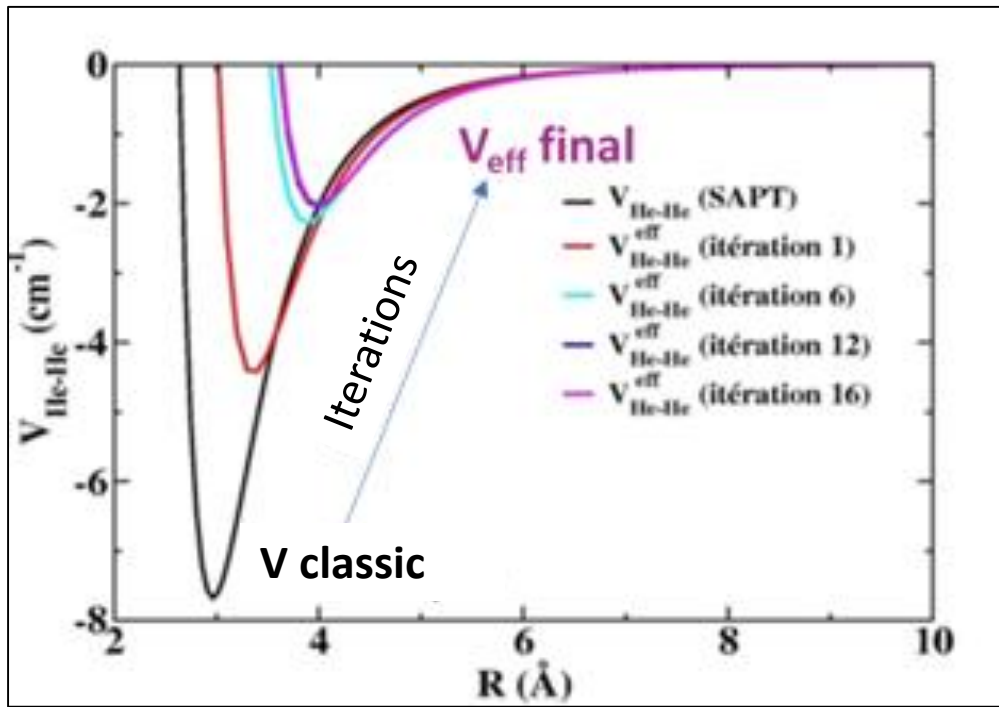
- Lowering well depth (Approximation of Zero Point Energy)
- Increasing of <R> from 3 to 4 Å (density correction)
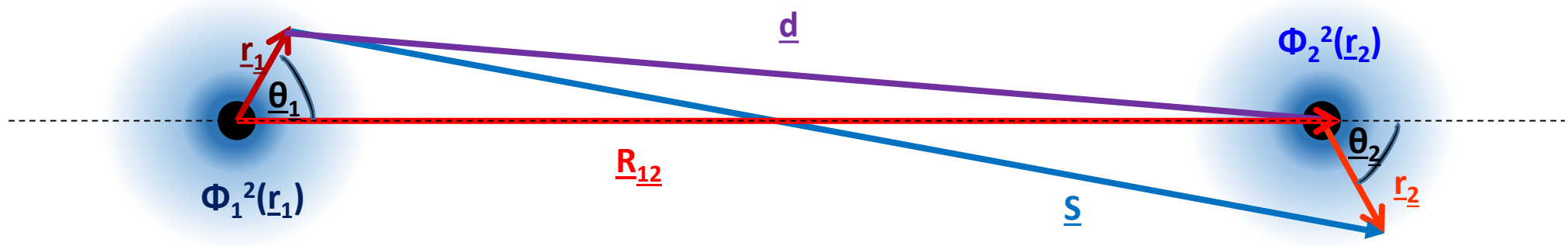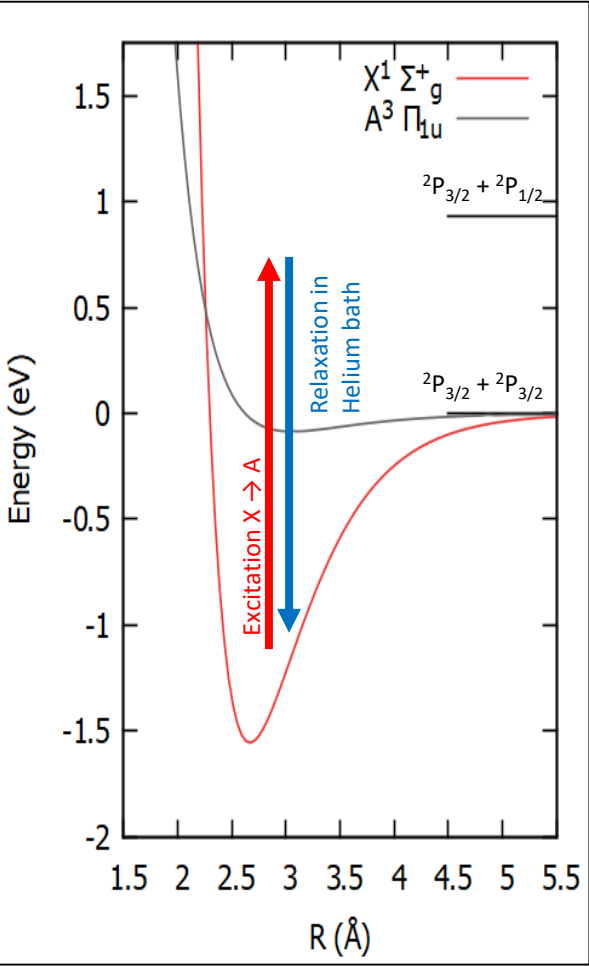
The dissociation energy for our I_2 model is about 1.55 eV according the first graph above. We performed some calculations for excitation energies below this threshold which correspond to vibrational excitation of I_2 without bond breaking. At higher excitation, we assume very rapid conversion from a A state continuum state into a X state continuum state, as was done in earlier model calculations [1].

- **Simulation of the photodissociation of I_2** inside a **helium** cluster (T= 0,5 K)
- **Method :** Quantum effective potential and semi-classical Zero Point Average Dynamic

Vibrational excitation at 0.77 eV   Electronic excitation at 1.55 eV   Electronic excitation at 2.13 eV
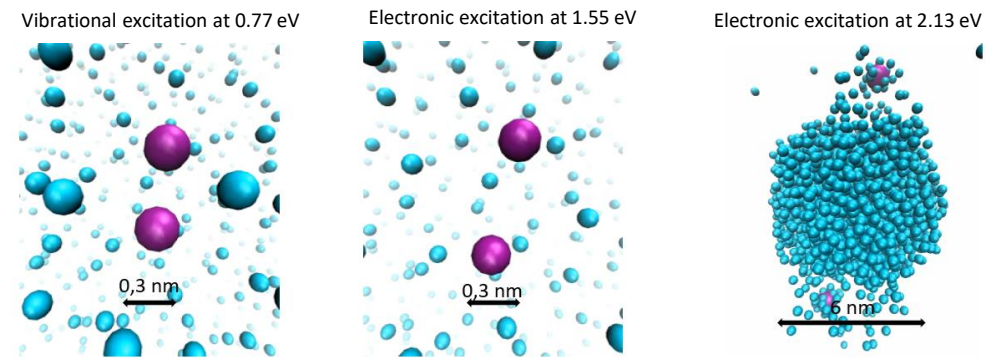

- Fragmentation limit of I_2 : 1.55 eV

The picture above illustrates the different outcomes depending on the energy deposited in the I_2 molecule. In the first two cases, iodine remains inside the He cluster. At 0.77 eV (about 50% of the dissociation energy) we observe damped vibrational motion. At 1.55 eV, exactly the iodine fragmentation limit, the molecular bond is broken and we observe energy dissipation followed by iodine atom recombination and return into a vibrational regime. Exciting iodine at 2.13 eV leads to fragmentation and fragment atoms leaving the cluster with a partial helium solvent shell.

These fragments can be experimentally observed by velocity imaging techniques. In our calculations we are able to identify two scenarios: Free IHe_N fragments above an exit threshold and trapped fragments (cage effect). This corresponds to photofragment size distributions observed for CF_3I under similar excitation conditions [3].

The graph at the lower left shows that the number of helium slowly drops with increased excitation energy, mostly due to energy flow into the helium bath and local thermal expansion. The number of neighbors starts to drop more visibly only upon substantially exceeding the molecular dissociation threshold of about 1.55 eV and the threshold which allows the escape of the photofragments from the droplet is somewhere near 2 eV.

The graph below displays the energy dissipation for a simulation of an excitation at 2.33eV (532 nm by a Nd-YAG laser) . The main observation is that photofragments lose an important part of their excess energy within a picosecond. Details of this fast relaxation mechanism will be studied in the future.
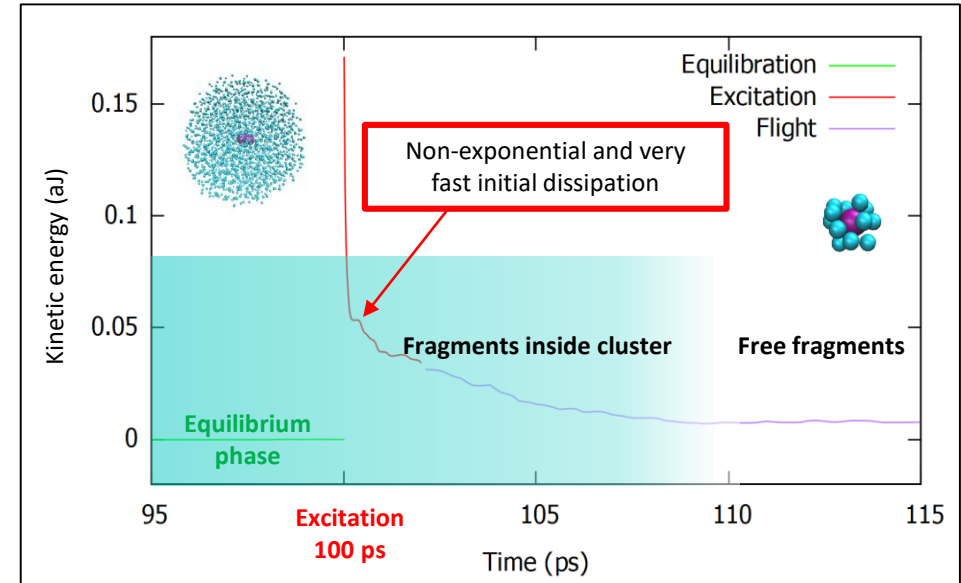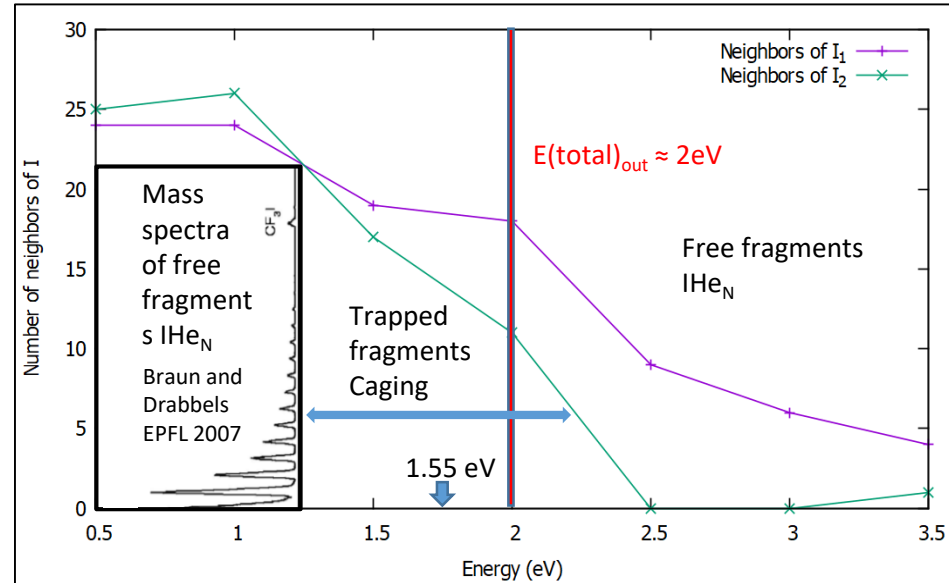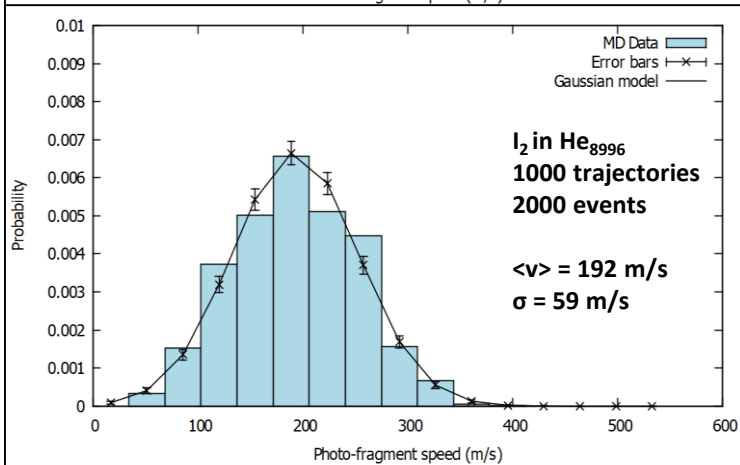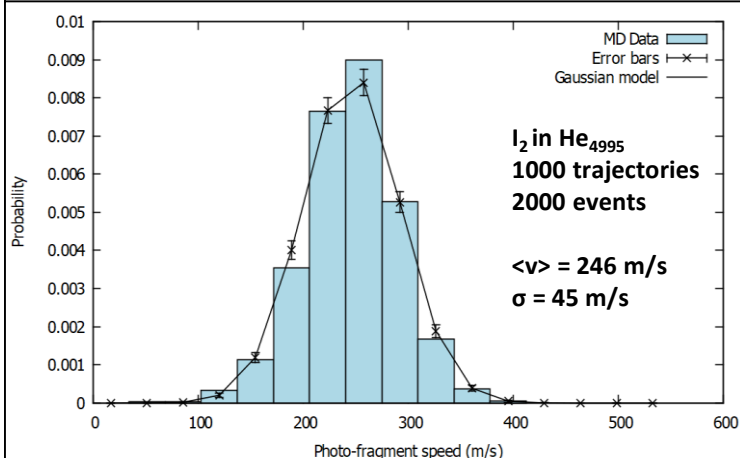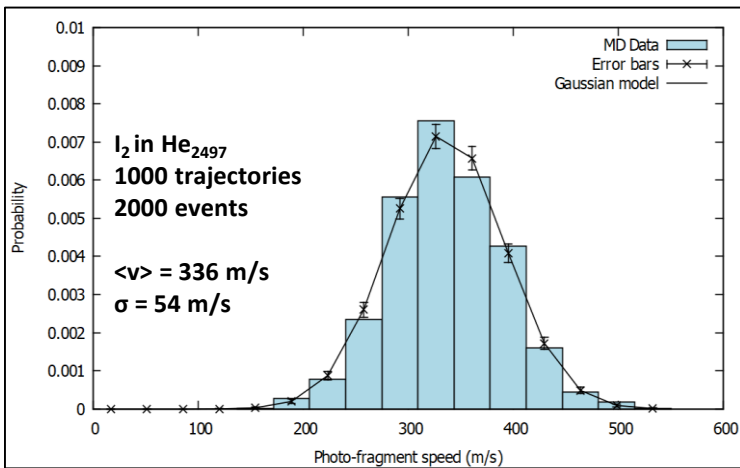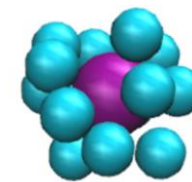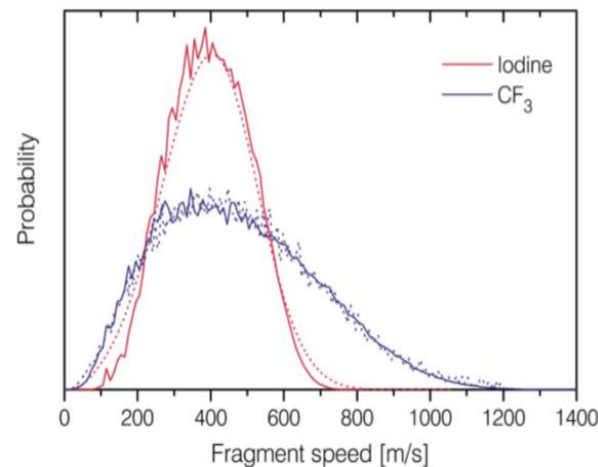
We ran 1000 independent photodissociation trajectories with an excitation energy of 2.33 eV corresponding to a realistic experiment using a frequency doubled Nd:YAG laser operating at 532 nm. Each dissociation event gives rise to two photofragments containing an iodine atom and a variable number of helium atoms with a distribution of exit velocities. The fragment size (right column) and exit velocity distributions (left column) vary clearly depending on the droplet size.

The black lines and error bars indicate count rates and estimated error bars for a Gaussian distribution with the same mean and standard deviation.

The main result is a shift of the photofragment velocity distribution to lower values with increasing nanodroplet size and a simultaneous evolution of the fragment sizes towards larger values. Unfortunately, there are no experimental results for our molecular system but the velocity ranges compare well with the observations of Braun and Drabbels.

Similar to the Ref [3] we calculate the kinetic energies of the photofragments from the simulations irrespective of the number of helium atoms attached and we obtain $E_{kin,I}$= 740 cm^{-1}, 424 cm^{-1}, and 290 cm^{-1} for the droplets with 2500, 5000, and 9000 atoms, respectively. These data are in the same range as the ones of Braun and Drabbels.

I$_2$ in He$_{2497}$
1000 trajectories
2000 events

<v> = 336 m/s
σ = 54 m/s

I$_2$ in He$_{4995}$
1000 trajectories
2000 events

<v> = 246 m/s
σ = 45 m/s

I$_2$ in He$_{8996}$
1000 trajectories
2000 events

<v> = 192 m/s
σ = 59 m/s

I$_2$ in He$_{2497}$
1000 trajectories
2000 events

<n> = 6.4 He
σ = 2.4 He

I$_2$ in He$_{4995}$
1000 trajectories
2000 events

<n> = 9.3 He
σ = 2.4 He

I$_2$ in He$_{8996}$
1000 trajectories
2000 events

<n> = 13.2 He
**σ = 2.9 He**

Iodine in He atom shell

Experimental speed distribution observed after CF$_3$I photodissociation from an excitation at 266 nm by Braun and Drabbels EPFL 2007
Size range 2000 – 20 000 atoms
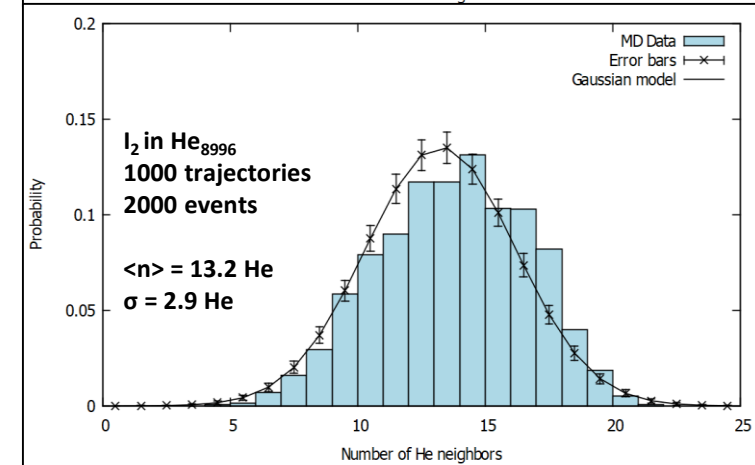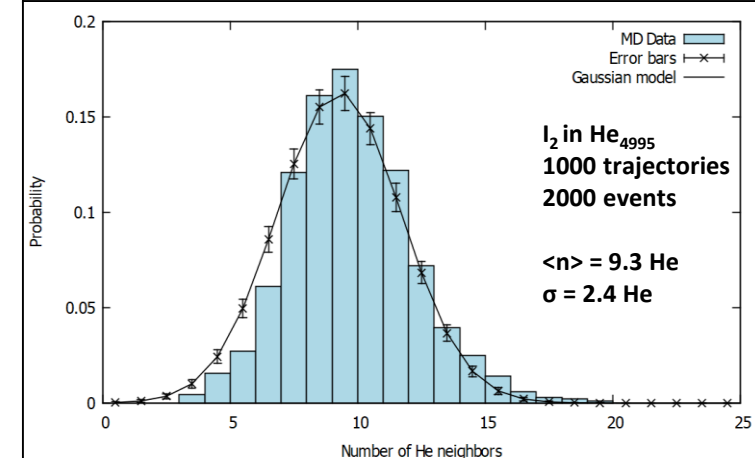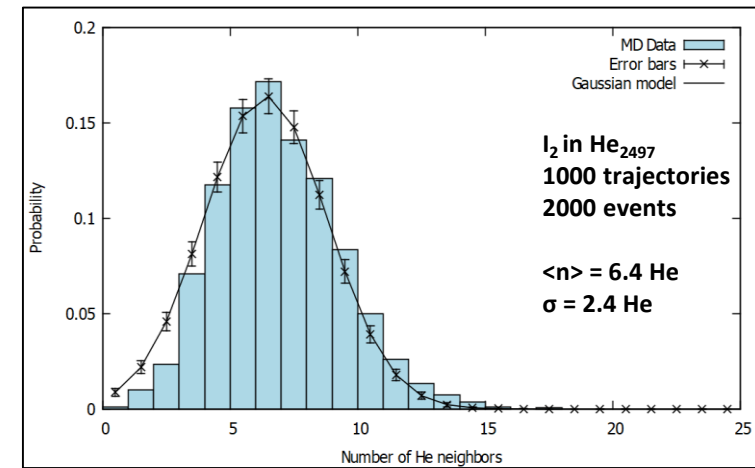
Conclusion and outlook

We have calculated several dynamic observables which have been seen in analogous experiments. The cage effect observed by experimentalists has been identified during our simulations. In terms of number of helium atoms attached to the iodine in the photo fragment and the velocities of the latter for non rotating helium nanodroplets the results are comparable with the experiments observations of Braun and Drabbels. We hope that our theoretical predictions will motivate an experimental investigation of iodine molecules in helium nanodroplets at the excitation energies considered in this work. Plenty of outlooks become possible theoretically as the helium nanodroplet rotation. How is the influence of that phenomenon on photodissociation ? We have begun some computer experiments on this. Moreover, the mechanism of doping by the first step of implantation and then the aggregation/recombination is an ongoing study.
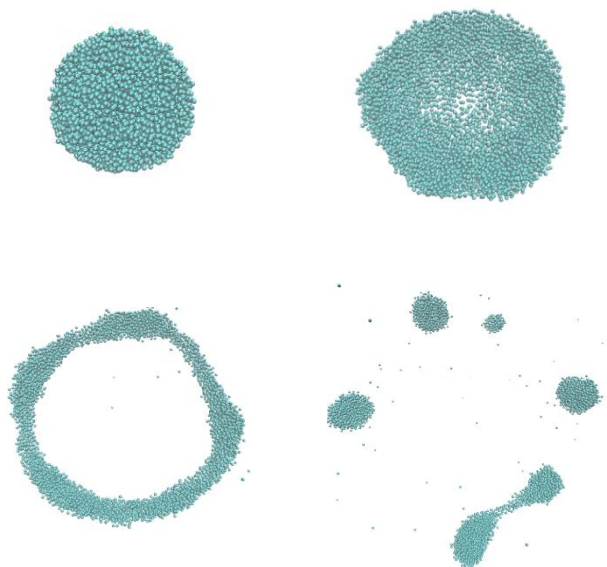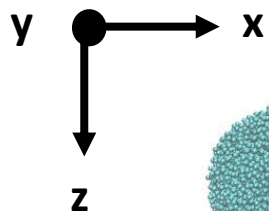
- Rotational excitation (**L=16ℏ/He atom**) of a helium droplet of 5000 atoms (left).

- Evolution of the distance between two xenon atoms implanted in a sequence of atom-cluster collisions on He_{5000} (without cluster rotation). The xenon atoms approach each other but before the final recombination to Xe_2 a long lived metastable situation with a thin layer of helium between the xenon atoms is clearly visible (right).
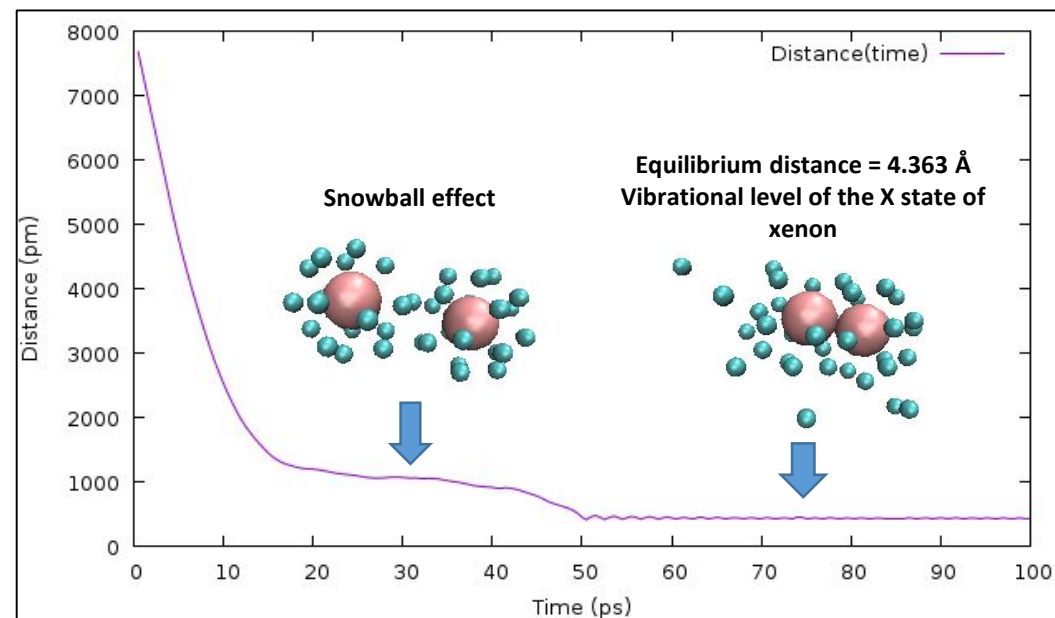
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