

System	C_6 (a.u.)	C_{12} (a.u.)
$Li + Li$	1394	1521.8e-6
$Cs + Cs$	6891	1271.2e-6

TABLE I. C_6 Van der Waals coefficients and well depths D_e for Li_2 [2] and Cs_2 [3].

I. ATOM + MOLECULE SCATTERING

A. General approach

As already discussed, due to the large number of available rovibrational states, doing a full multichannel quantum mechanical study of a reaction even between something as simple as a dimer and an atom can be a very complex problem, almost impossible to solve with nowadays capabilities. However, as observed by Croft and Bohn [1], many of the features and observables of a collision between a molecule and a dimer, such as its chaotic behavior or scattering rate, can be computed by using a purely classical approach. This poses a much more tractable problem, both analytically and computationally.

To perform the classical computation we assume that the interaction is purely determined by a pairwise-additive Lennard-Jones potential

$$(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_{i \neq j} \frac{C_{12}}{(\mathbf{r}_i - \mathbf{r}_j)^{12}} - \frac{C_6}{(\mathbf{r}_i - \mathbf{r}_j)^6}, \quad (1)$$

where C_6 is the leading order van der Waals coefficient, and the higher order C_{12} is chosen in order to obtain the correct atom-atom well depth, as given by $D_e = C_6^2/4D_e$. Other effects such as contributions due to the spin of the atoms are ignored and the values of the van der Waals coefficients used are summarized in Table I, where the atom species are chosen such as to span a wide range of possible atomic atoms (they are also alkali metals, which are extensively used in ultracold gases experiments). From the potential energy we can readily compute the forces acting on the atoms, $\mathbf{F} = -\nabla V$, from which we can use Newton's laws to propagate the atoms in time. **This last sentence is clunky. Maybe change it?**

An exaggerated version of the Lennard-Jones potential is given in Fig. 2, together with the basic setup of the collision's initial conditions. We thus distinguish the orientation of the dimer in the XZ-plane, θ_0 , the initial velocity of the incoming atom (in the rest frame of the dimer), as given by the initial temperature T , and the impact parameter, b , as some of the initial condition variables we can tune in order to analyze the collision. As already mentioned, we can also consider different atomic species, which changes the masses and the interaction strengths.

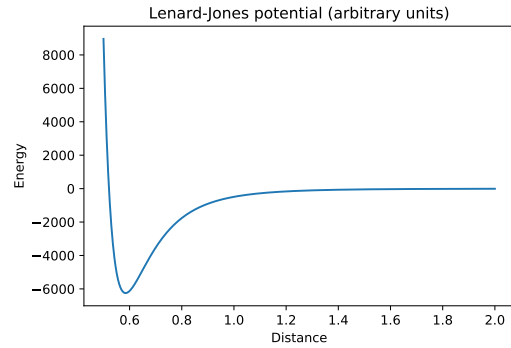
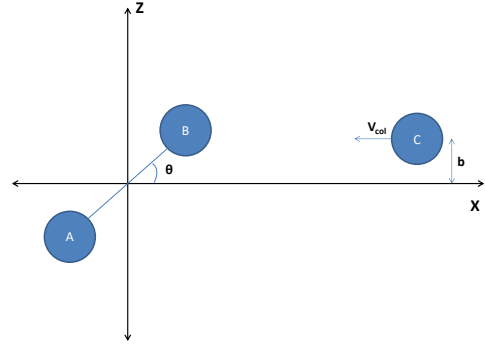


FIG. 1. Top: Schematic of atom-dimer collision, including all the initial conditions variables. Bottom: Model of Lennard-Jones atom-atom pair potential.

B. Numerical methods

Talk about integrator used and maybe a quick tabel for convergence (change step size or delta t by a factor 2 and calculate some residual in the trajectory or check wehtehr the basin has changed).

C. Complex lifetime

One of the main observables of interest in ultracold collisions is the complex' lifetime (or the related quantity of scattering rate), which can provide information about the ergodicity of the reaction and can also be cross-checked with other methods of analyzing the collision. **Relate this to what Jessie did. I didn't quite get Fig. 2, which may be interesting and should be easy to get, if anyone else wants to do it. There is some code to do it. Otherwise, we should be fine; we don't have to replicate everything...** To this end, we compute the lifetime of the reaction as the time between the initial starting point (the atom starts $r_{\text{init}} = 60a_0$ away from the dimer, where a_0 is the Bohr radius and the equilibrium distance between the dimer's atoms is $\bar{a} = 8.78a_0$ and the time when the hyper-radius $\sqrt{R_{AB}^2 + R_{BC}^2 + R_{AC}^2}$ is first greater than r_{init} . We note

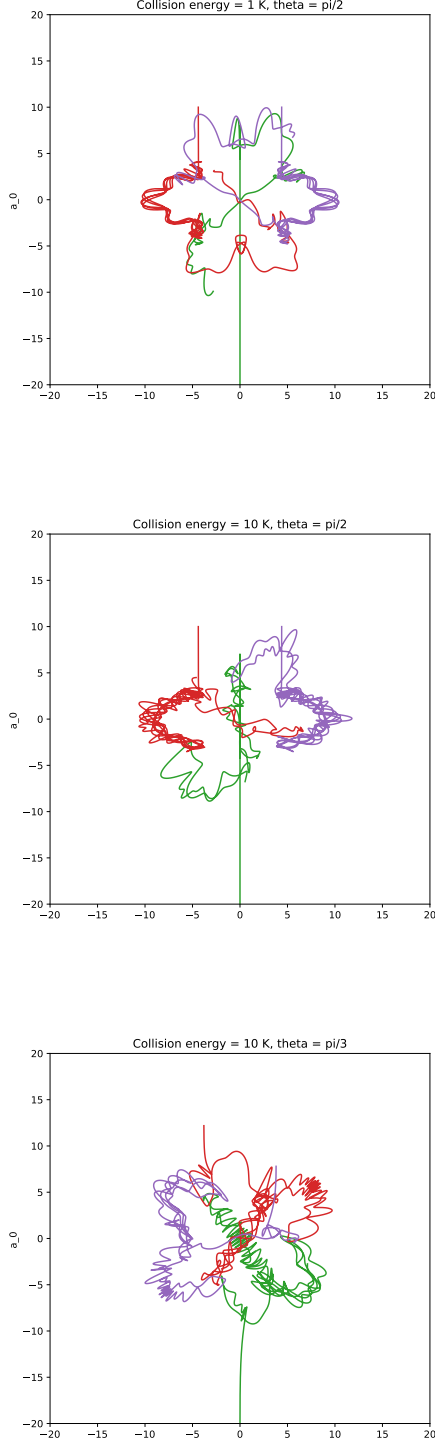


FIG. 2. Top: Schematic of atom-dimer collision, including all the initial conditions variables. Bottom: Model of Lennard-Jones atom-atom pair potential.

that different methods of timing the reaction are possible, but they should not change the functional behavior of the lifetime. In particular, we analyze the dependence of the lifetime as a function of the collision energy for two atom species, as shown in Fig. 7. We observe that lifetime has a power-law dependence on the initial energy, with exponent -0.47 for $\text{Li} + \text{Li}_2$ and -0.50 for $\text{Cs} + \text{Cs}_2$.

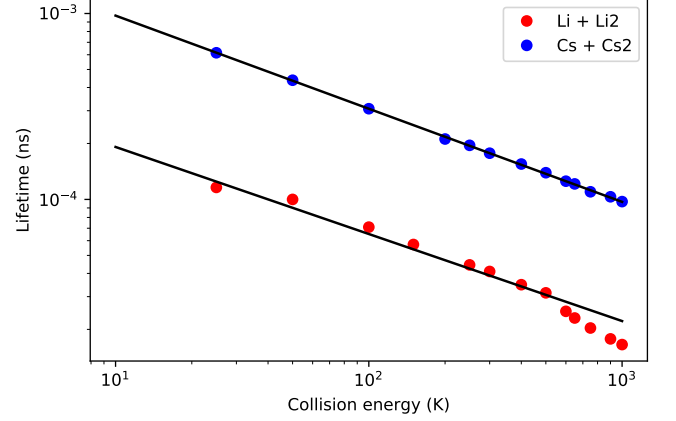


FIG. 3. Lifetime as a function of the collision energy for the atom-dimer cases of $\text{Li} + \text{Li}_2$ and $\text{Cs} + \text{Cs}_2$. The dots represent the computed total time that the atom-dimer pair spend in the reaction, while the solid line represents a power-law fit.

Maybe talk about ergodicity and applicability of RRKM but, again, I think this is more what Jessie did so maybe she will mention it. Otherwise can summarize page 4 from Bohn's paper here.

D. Chaos

An interesting feature of atomic-dimer dynamics at ultracold temperatures is the onset of chaos, which arises as the atoms get closer together in low-energy regimes and the interactions get stronger. We can observe the chaotic behavior by analyzing the outcome of trajectories as a function of the initial conditions. We thus vary θ , the angle of orientation of the dimer with respect to the velocity of the incoming atom, and look at both the lifetime of the trajectory as well as what "kind" of trajectories they are: similar to what Croft and Bohn did, we use the fact that this is a classical collision and can therefore label each atom involved; we thus classify trajectories by whether the two initial atoms forming the dimer stayed together ($\text{AB} + \text{C}$), whether they changed partners ($\text{AC} + \text{B}$ or $\text{BC} + \text{A}$), or whether the complex broke apart with all three atoms flying apart independently ($\text{A} + \text{B} + \text{C}$).

The results for $\text{Li} + \text{Li}_2$ at $T = 350$ K are summarized in Fig. 1D. We conclude that, while there are regions of relative stability, both the lifetime and the ending "basin"

can vary wildly as a function of θ . Even more compelling, by "zooming in" on a region of θ we qualitatively observe the same features, so we conclude that the system exhibits the scale invariance characteristic of fractals.

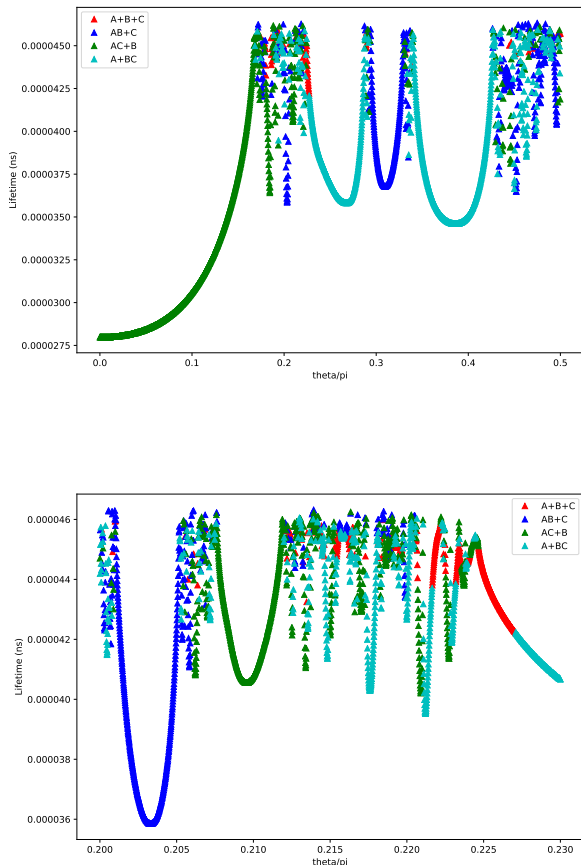


FIG. 4. Lifetime and ending "basin" for Li+Li₂ at $T = 350$ K as a function of the initial orientation angle of the dimer θ . The lower panel is a zoomed in version of the upper one, illustrating the scale invariance property of the system.

The fractal dimension [4] characterizes how much the fractal pattern changes as one changes the scale of the system, so it is a way to quantify the scale invariance and, as we shall see, also the moment of onset of chaos. As already discussed, we classify trajectories by the "basin" they end up in. A trajectory is further classified as unstable under perturbation of initial conditions if by chang-

ing the initial variables by a value δ the outcome ends being part of a different basin than the original one. As such, we compute a large number of pair of trajectories, in each pair the partners having the initial conditions (in our case, the orientation angle θ) differ by an amount δ . We then compute the fraction of unstable trajectories, which is observed to be characterized by the uncertainty algorithm [5]

$$f(\delta, E_{\text{col}}) \propto \delta^{\alpha(E_{\text{col}})}, \quad (2)$$

where E_{col} is the collision energy, δ is the perturbation we apply (to the angle θ), and α is the uncertainty exponent that we fit.

Figure 5 illustrates some of the results for a wide range of temperatures, from which we can conclude that at high collision energies the trajectories are essentially stable under perturbation, with the unstable fraction decreasing as δ gets smaller, while for lower collision energies the unstable fraction is essentially independent of δ , meaning that there is no correlation between the outcomes of trajectories that are arbitrarily closely "neighboring" in the phase space of initial conditions.

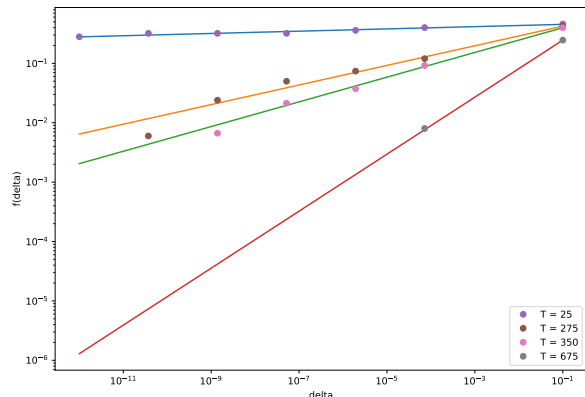


FIG. 5. The unstable fraction of trajectories, $f(\delta)$, as a function of the perturbation value δ for Li+Li₂. At 25 K α is 0.02, corresponding to trajectories that are completely sensitive to initial conditions' perturbations, while at 250 K and 675 K it is 0.2 and 0.48, respectively.

Quickly talk about fractal dimension...

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- [1] J. F. E. Croft and J. L. Bohn, *Physics Letters A* **89** (2014).
 - [2] N. S. Dattani and R. J. L. Roy, *Journal of Molecular Spectroscopy* **68** (2011).
 - [3] F. Xie, V. B. Sovkov, A. M. Lyyra, D. Li, S. Ingram,

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- [4] B. Mandelbrot, *Science* **636** (1967).
- [5] S. W. McDonald, C. Grebogi, E. Ott, and J. A. Yorke, *Physica D* **17** (1985).

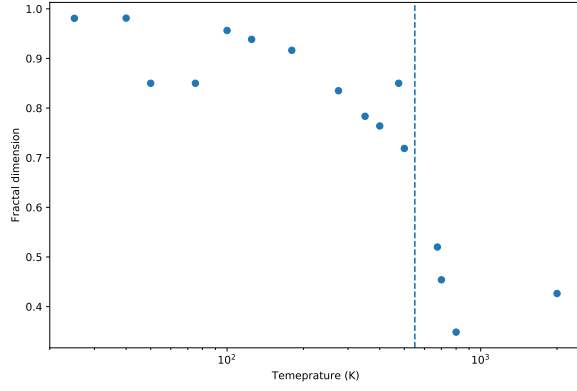


FIG. 6. Fractal dimension d as a function of the collision energy of $\text{Li} + \text{Li}_2$. The vertical line marks the approximate energy at which chaotic behavior ensues.

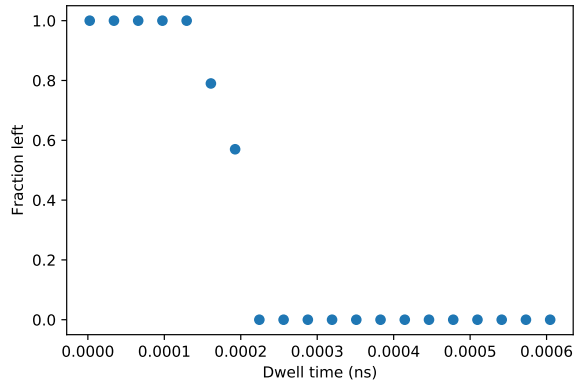


FIG. 7.