Supplementary Material: Reaction Rates in Nitromethane under High Pressure from Density Functional Tight Binding Molecular Dynamics Simulations

Romain Perriot,*,† M. J. Cawkwell,† Enrique Martinez,† and Shawn D. McGrane‡

†*Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

‡*Shock and Detonation Physics, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA*

E-mail: rperriot@lanl.gov

Decorrelation of the initial configurations

In most cases, the atomic configuration of the system is the same at the beginning of each $\rho - T$ run, when different random seeds are then applied to assign the initial velocities and for the Langevin algorithm. In order to demonstrate that the systems quickly become independent realizations, we have calculated the cross-correlation coefficient[1,2] C_α for the distance between two atoms belonging to different molecules (we chose carbon atoms):

$$C_\alpha(dt) = \frac{< \mathbf{r}_{ij}(t) \cdot \mathbf{r}_{ij}(t+dt) >}{\left(< \mathbf{r}_{ij}(t) >^2 < \mathbf{r}_{ij}(t+dt) >^2 \right)^{1/2}}, \tag{S1}$$

where the average is taken over all pairs of atoms $i, j \neq i$ and all intervals of length dt. For each pair, the minimum distance between i and each of the images of j through the periodic

boundary conditions was used to define $\mathbf{r}_{ij}(t) = \big(x_j(t) - x_i(t), y_j(t) - y_i(t), z_j(t) - z_i(t)\big)$. By construction, C_α goes from +1 (maximum correlation) to -1 (anti-correlation).[1] Any value of the cross-correlation coefficient between 0.3 and -0.3 is generally accepted as the criterion characterizing the two quantities as not correlated.[3]

The results for C_α are shown in Fig. S1, for four representative cases considered in our study: low ρ/low T, high ρ/low T, low ρ/high T, high ρ/high T. For all cases, we see that C_α decreases rapidly over the first few ps, while a non-zero tail may or may not be observed. Regardless, for all systems the time τ at which $C_\alpha < 0.3$ is less than 4 ps. This is less than the duration of the NVT thermalization, and less than 1/4 of the lowest average ignition time reported in our study (17 ps, for the highest density and temperature, ρ=2.325 g.cm^3 and T=1800 K). We thus conclude that all samples, starting from the same atomic configuration, quickly "forget" their origin and that the data reported in the paper indeed corresponds to independent realizations of the system.

Ignition and explosion data

Ignition and explosion time data, with average and fit, not shown in Figs. 6 and 7 in the paper are presented here. The averaged data is fitted to:

$$t_{\mathrm{adb}}(T) = \frac{A\ {T_0}^2}{T_a}\ \exp\!\left(\frac{T_a}{T_0}\right). \tag{S2}$$

The fitting coefficients A and T_a are reported in Table 2 in the paper.

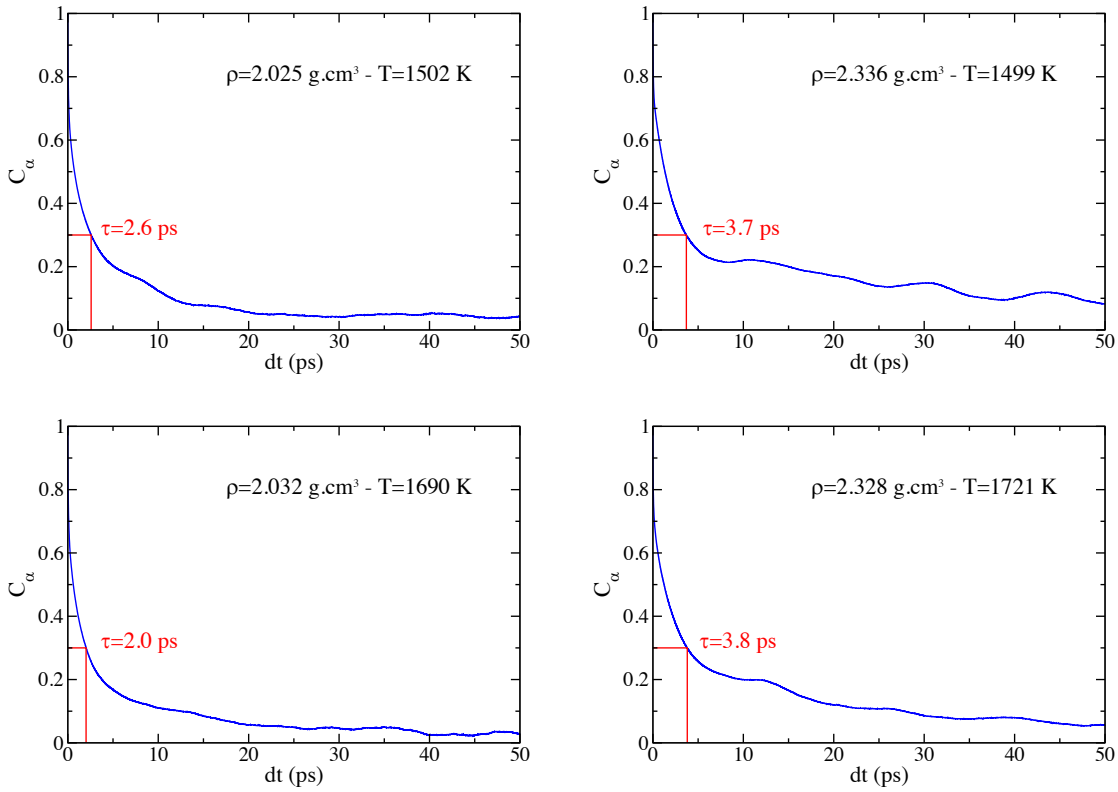

Figure S1: Cross-correlation coefficient C_α (Eq. S1), for four representative cases used in our study (due to short ignition times, there is little data that can be used at T>1700 K). In red, we report the time τ at which C_α falls below 0.3 and the system is considered uncorrelated.

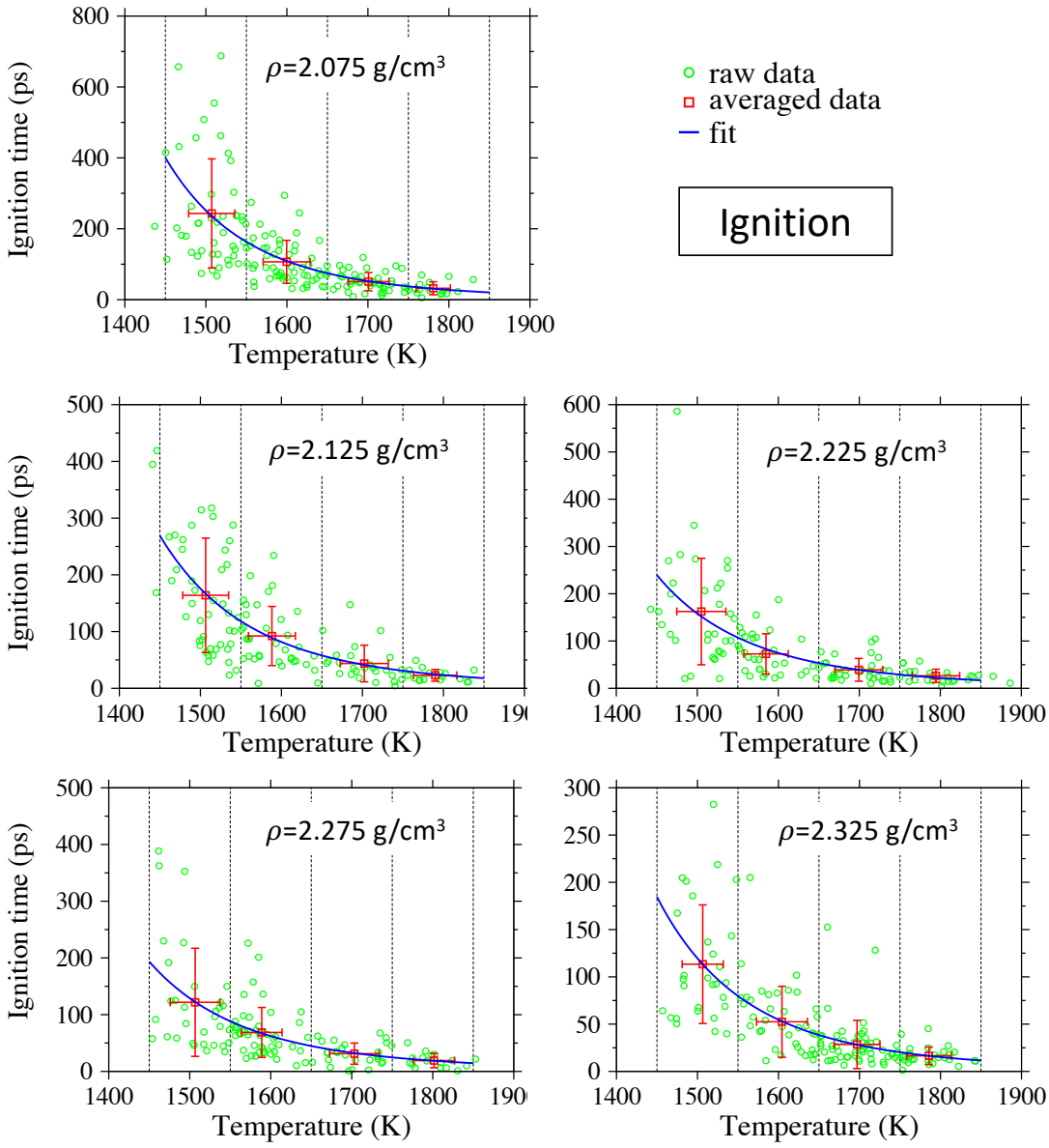

Figure S2: Ignition times extracted from MD runs, as a function of density and temperature for ρ=2.075, 2.125, 2.225, 2.275, and 2.325 g/cm^3: raw data, averaged data over 100 K bins (see Table 2 in the paper), and fit using Eq. S2.

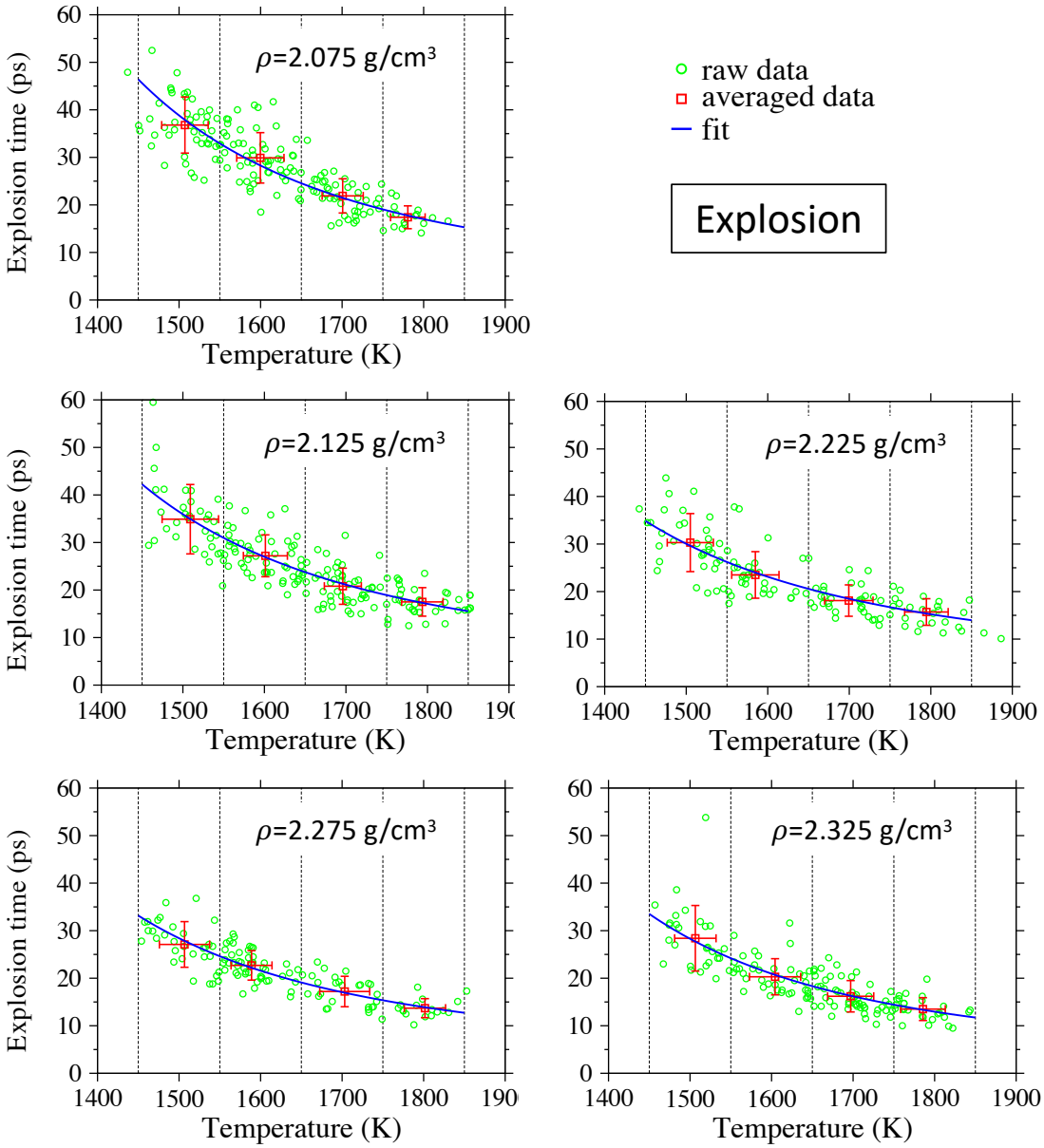

Figure S3: Explosion times extracted from MD runs, as a function of density and temperature for ρ=2.075, 2.125, 2.225, 2.275, and 2.325 g/cm^3: raw data, averaged data over 100 K bins (see Table 2 in the paper), and fit using Eq. S2.

References

(1) Kormos, B. L.; Baranger, A. M.; Beveridge, D. L. A Study of collective atomic fluctuations and cooperativity in a U1A-RNA complex based on molecular dynamics simulations. *J. Struct. Biol.* **2007**, *157*, 500–513.

(2) Brooks III, C. L.; Karplus, M.; Montgomery Pettitt, B. *Proteins: A Theoretical Perspective of Dynamics, Structure, and Thermodynamics*; Advances in Chemical Physics Vol. LXXI; John Wiley & Sons, 1988; Chapter XI.

(3) Ramachandran, K. M.; Tsokos, C. P. *Mathematical Statistics with Applications*; Academic Press, 2009; Chapter 8.