Analysis and Interpretation of First Passage Time Distributions Featuring Rare Events

Supplementary Information

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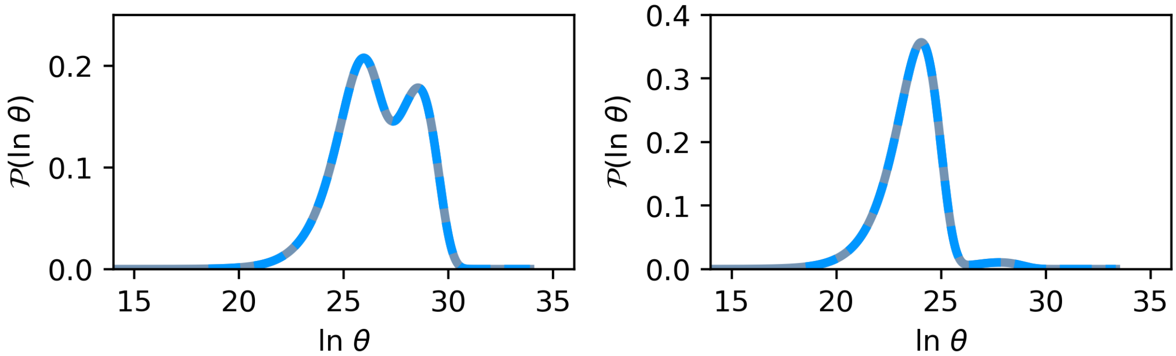

FIG. 1. First passage time distribution for the nine community network described in the main text,[1] where the source and sink are singular minima that lie at the bottom of two different trapping basins. The distribution is computed using eigendecomposition at $k_bT = 1$, for the full 994 state network (grey) , and a pGT network where only the nine states at the bottom of trapping basins are retained (blue). Both distributions are identical, which shows that long time peaks can be well preserved by retaining only states at the bottom of trapping basins.

[1] Phil. Trans. Roy. Soc. A 10.1098/rsta.2022.0245.

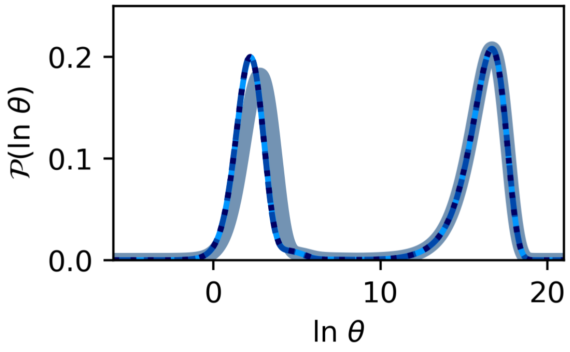

FIG. 2. First passage time distribution for the LJ_{38} cluster, as shown in the disconnectivity plot in Figure 9 in the main text, from a high energy minimum to the sets $\mathcal{A}$ (left) and $\mathcal{B}$ (right) at $k_bT/\epsilon = 0.14$, where ϵ is the pair well depth. When we retain more states under pGT, the FPT distribution converges. We show data for four different sets of retained states where we keep the minima with the highest 2500 (grey) , 3000 (light blue) and 3500 (blue) equilibrium occupation probabilities in the first- and second-neighbour sets, alongside the fastest path itself, as described in more detail in the main text. We also show the FPT distribution obtained from retaining the set of minima with the highest 3000 equilibrium occupation probabilities in the first- and second-neighbour sets, plus the 500 highest from the third-neighbour set and the fastest path (dark blue). This selection converges at around 3000 states, where there are only small changes from the FPT distribution from 2500 states.

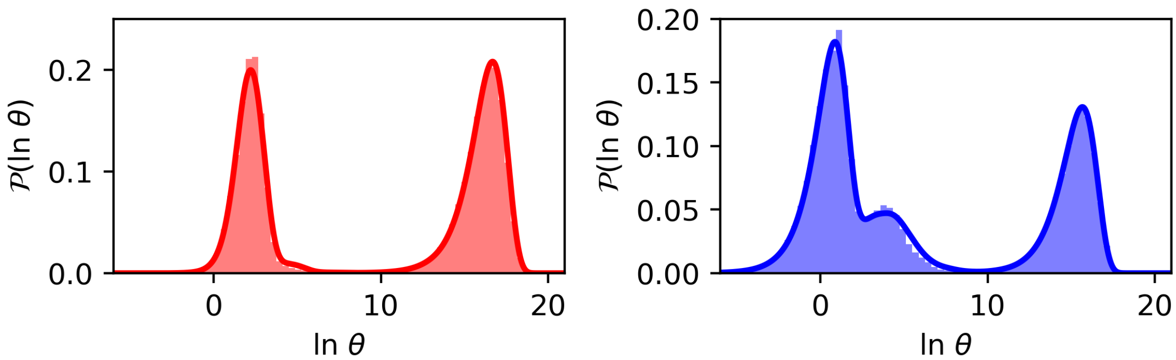

FIG. 3. First passage time distributions for the LJ_{38} cluster, as shown in the disconnectivity plot in Figure 9 in the main text, from a high energy minimum to the sets $\mathcal{A}$ (left) and $\mathcal{B}$ (right) at $k_bT/\epsilon = 0.14$ where ϵ is the well depth. We compare results from kinetic Monte Carlo (histogram) and the converged first passage time distribution from pGT and eigendecomposition from Figure 2 (line). The converged FPT from the 3006 state system is closer to the FPT generated from kMC than for the 2506 state system shown in Figure 8 in the main text, at the expense of a longer computation time.

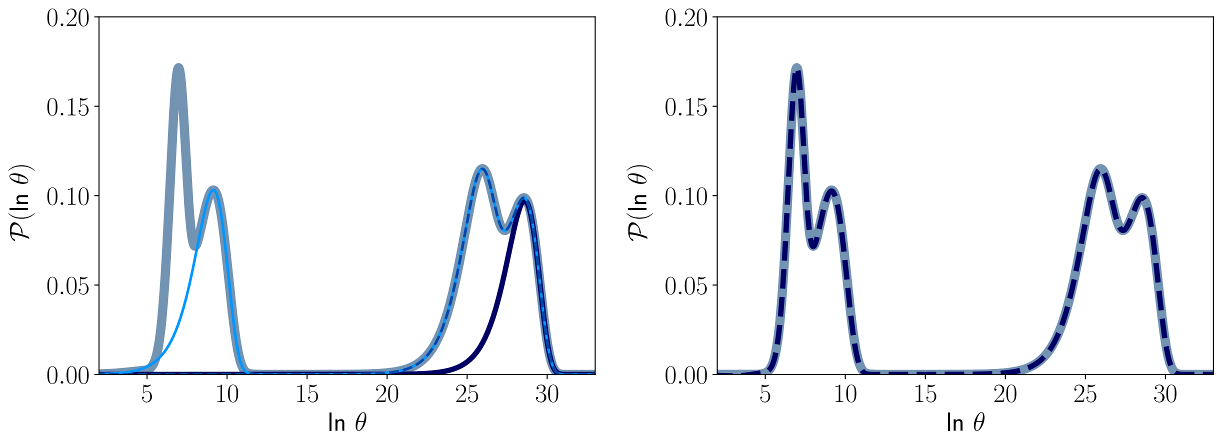

FIG. 4. First passage time distributions computed using a summation over a subset of eigenmodes, for the full 9 trap system $\mathcal{A} \leftarrow \mathcal{B}$ transition described in the main text. Left: Summation performed over the eigenmodes with the smallest magnitude eigenvalues, showing the smallest number of modes summed in eigenvalue order that are required to retain the four peaks. Smallest eigenvalue mode only (dark blue), five smallest (dashed blue), 12 smallest (thin light blue) and the 234 smallest (thick grey). Right: Summation performed over the eigenmodes with the largest $|A_\ell|$ values. Only 40 eigenmodes (dashed dark blue) are required to produce the full distribution computed from all eigenmodes (grey).

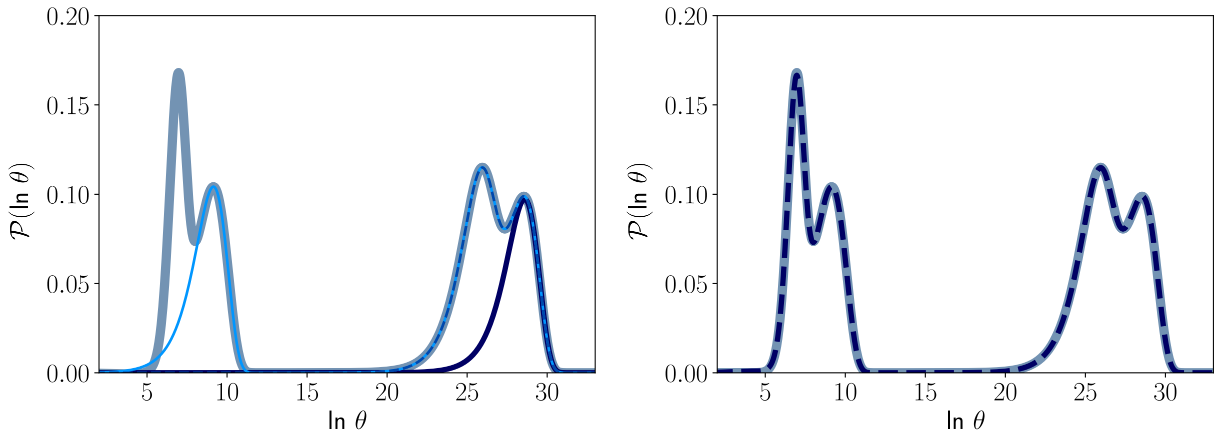

FIG. 5. First passage time distributions computed using a summation over a subset of eigenmodes, for the pGT reduced 9 trap system $\mathcal{A} \leftarrow \mathcal{B}$ transition described in the main text. Left: Summation performed over the eigenmodes with the smallest magnitude eigenvalues, showing the smallest number of modes summed in eigenvalue order that are required to retain the four peaks. Smallest eigenvalue mode only (dark blue), five smallest (dashed blue), 9 smallest (thin light blue) and the 39 smallest (thick grey). Right: Summation performed over the eigenmodes with the largest $|A_\ell|$ values. Only 28 eigenmodes (dashed dark blue) are required to produce the full distribution computed from all eigenmodes (grey).

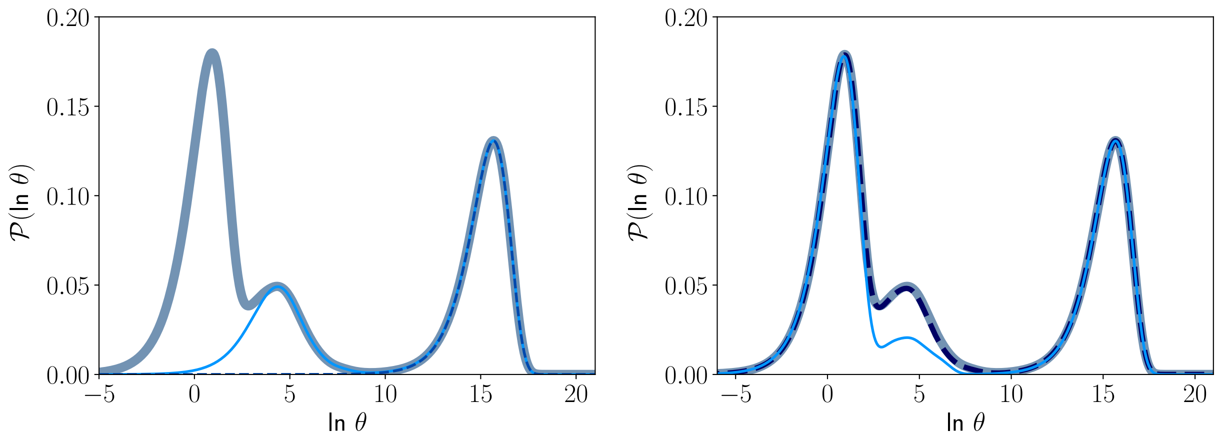

FIG. 6. First passage time distributions computed using a summation over a subset of eigenmodes, for the pGT reduced LJ_{38} system, with relaxation to $\mathcal{B}$ as described in the main text. Left: Summation performed over the eigenmodes with the smallest magnitude eigenvalues, showing the smallest number of modes summed in eigenvalue order that are required to retain the four peaks. 21 smallest (dashed blue), 1124 smallest (thin light blue), and the 1934 smallest (thick grey). Right: Summation performed over the eigenmodes with the largest $|A_\ell|$ values. Only 200 eigenmodes (dashed dark blue) are required to produce the full distribution computed from all eigenmodes (grey). The second peak is the last to converge, the first 20 eigenmodes (thin light blue) in this summation are sufficient to converge the first and last peak.

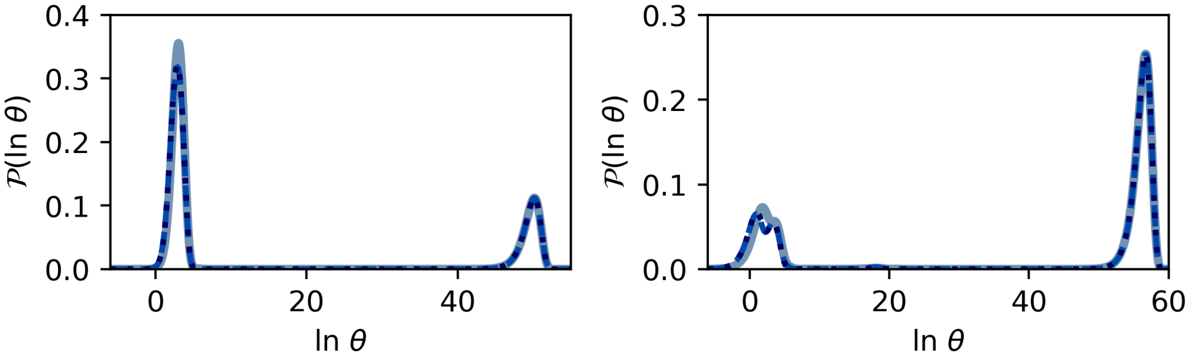

FIG. 7. First passage time distributions for the LJ_{38} cluster, as shown in the disconnectivity graph in Figure 9 in the main text, from a high energy minimum to the sets $\mathcal{A}$ (left) and $\mathcal{B}$ (right) at $k_bT/\epsilon = 0.06$, where ϵ is the well depth. Here we compare results using different sets of retained states, namely the original 2506 states used for Figure 8 in the main text (grey line), and the set of 3006 states used in Figure 3 (dashed blue line), where both state sets were computed by converging the first passage time distribution at $k_bT/\epsilon = 0.14$. We additionally show the FPT distribution obtained from retaining 3503 states obtained by running Dijkstra's shortest path algorithm to identify the fastest path at $k_bT/\epsilon = 0.06$ (dashed dark blue line). We find that the FPT has converged when we retain the 3500 states with the highest equilibrium occupation probabilities within the first- and second-neighbour lists, along with the fastest path itself. This results shows we can use the same set of retained states over a range of temperatures.

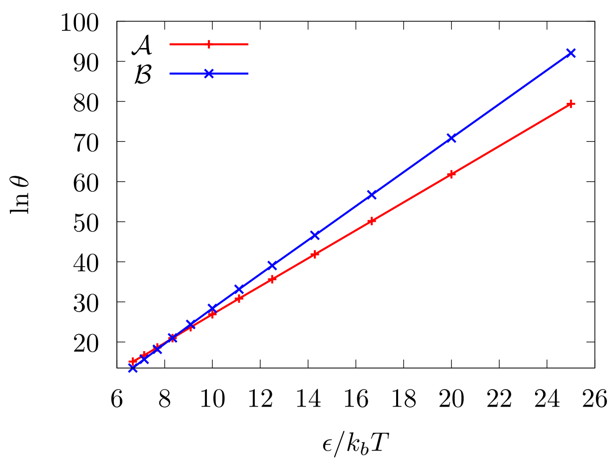

FIG. 8. Position of the slow peak in the first passage time distribution as a function of temperature for the LJ_{38} database renormalised down to 2506 states. For relaxation to both the $\mathcal{A}$ and $\mathcal{B}$ minima the dependence is close to an Arrhenius form.