Coupled linear and rotary motion in supramolecular helix handedness inversion

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Electronic Supplementary Information

I. MODEL

In the present work the asymmetric dipolar dumbbells are modelled using multiple interaction sites. Each dumbbell involves two spherical lobes, modelled by Lennard-Jones (LJ) sites and a point-dipole directed across the axis between the lobes, within a rigid-body framework.[1] The total energy of a system of N dumbbells in an electric field $\boldsymbol{E}$ is

$$\begin{aligned} U &= \sum_{I=1}^{N-1}\sum_{J=I+1}^{N}\sum_{i\in I}^{1,2}\sum_{j\in J}^{1,2} 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \\ &+ \sum_{I=1}^{N-1}\sum_{J=I+1}^{N}\frac{\mu_D^2}{r_{IJ}^3}\left[(\hat{\boldsymbol{\mu}}_I\cdot\hat{\boldsymbol{\mu}}_J)-3(\hat{\boldsymbol{\mu}}_I\cdot\hat{\mathbf{r}}_{IJ})(\hat{\boldsymbol{\mu}}_J\cdot\hat{\boldsymbol{r}}_{IJ})\right]-\mu_D\sum_{I=1}^{N}\hat{\boldsymbol{\mu}}_I\cdot\boldsymbol{E}. \end{aligned} \quad (1)$$

Here, $\mathbf{r}_I$ is the position vector for the point-dipole on dumbbell I, $\hat{\boldsymbol{\mu}}_I$ is the unit vector defining the direction of the dipole moment, whose magnitude is μ_D, $\mathbf{r}_{IJ}=\mathbf{r}_I-\mathbf{r}_J$ is the separation vector between dipoles on dumbbells I and J with magnitude r_{IJ}, $\hat{\mathbf{r}}_{IJ}=\mathbf{r}_{IJ}/r_{IJ}$, and r_{ij} is the separation between LJ sites i and j. The units of energy and length are chosen as the LJ parameters ϵ_{11} and σ_{11}, respectively. For the LJ interactions we set $\epsilon_{11}=\epsilon_{22}=\epsilon_{12}=1$ and $\sigma_{11}=1$. $\sigma_{22}<1$ was varied to explore the effects of asymmetry with $\sigma_{12}=(\sigma_{11}+\sigma_{22})/2$.[2] With the lobes characterised as spheres with diameters σ_{11} and σ_{22}, $\alpha=\sigma_{11}/\sigma_{22}$ defines an asymmetry parameter. The direction of the electric field $\boldsymbol{E}=(0,0,E)$ was held fixed along the z-axis of the space-fixed frame as its strength, E, was varied. μ_D is then in reduced units of $(4\pi\epsilon_0\epsilon_{11}\sigma_{11}^3)^{1/2}$ and E is in $[\epsilon_{11}/(4\pi\epsilon_0\sigma_{11}^3)]^{1/2}$, where ϵ_0 is the permittivity of free space. The morphology of the global minima is sensitive to the asymmetry parameter α in particular, with even the number of strands for the helical global minima of a cluster of a given size dependant on α.[2] The sets of parameters considered in the present work ensure that the global minimum is a single helical strand. Although we restricted ourselves to a single α value in the present work, the inversion mechanism we report here is likely to be observed in the presence of relatively strong electric fields as long as the global minima consist of a single helical strand.

II. BASIN-HOPPING GLOBAL OPTIMISATION

We employed the basin-hopping[3,4] approach to identify the global minima. This method is based upon hypersurface deformation, where the transformation of the potential energy surface preserves the global minimum, and also the relative energies of the local minima. In practice, the configuration space is explored by taking steps, both translational and rotational. A local geometry optimisation follows each perturbation before the step is accepted or rejected on the basis of a Metropolis criterion based on the energy of the local minimum. Since the objective is to step out of the current minimum, step sizes are much larger than those typically used in Monte Carlo simulations. We accept a structure as the global minimum for a cluster if at least five different runs starting from random configurations at a given size produce the same lowest minimum. For the parameter sets considered in the present work, all the runs undertaken led to the same lowest energy structure, which was hit for the first time typically within a few thousand basin-hopping steps corresponding to less than 1% of the total length of the runs, suggesting that the configurational space is exhaustedly searched for all practical purposes.

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III. DISCRETE PATH SAMPLING

We used the discrete path sampling (DPS) approach,[5–8] a coarse-grained analogue of the transition path sampling method,[9–11] to characterise the fastest path between the global minima having opposite handedness. An initial path, consisting of a series of intervening transition states and minima on the underlying potential energy surface, was determined by double-ended transition state searches, which were performed with the doubly[12] nudged elastic band (DNEB) algorithm.[13–15] Here, a transition state is defined geometrically as a stationary point with a single negative Hessian eigenvalue.[16] The connectivity of a transition state is then defined by the two minima reached by (approximate) steepest-descent paths leaving parallel and antiparallel to the eigenvector corresponding to the unique negative eigenvalue; such a minimum-transition state-minimum triplet is termed an elementary rearrangement. The limited-memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS) algorithm of Liu and Nocedal was used for the local minimisation.[17,18] A set of discrete paths (*i.e.* connected sequences of minima and the intervening transition states on the potential energy surface) was generated systematically following the DPS approach from the initial connected path.[8] The objective here is to grow a database of connected stationary points starting from those in the initial path by adding all the minima and transition states found during successive connection-making attempts to construct discrete paths between pairs of minima selected from the current database. The discrete path that makes the largest contribution to the phenomenological rate constant for the handedness inversion within a steady-state approximation for the intervening minima was extracted from the DPS database using a network formulation[19] via Dijkstra's shortest-path algorithm.[20] The original DPS approach was presented in ref. 5, and more recent developments can be found in refs. 6–8.

IV. LEGENDS FOR SUPPLEMENTARY MOVIES

Supplementary Movie 1: Pathway for the reversal of handedness for a supramolecular helix with two perpendicular views. Evolution along the path, summarised in Figure 1, is shown for a helical strand, which is assembled from 13 asymmetric dipolar dumbbells in the presence of an electric field. The mechanism involves a boundary between two segments of opposite handedness, which we call a defect, propagating along the strand from one end to the other. The two segments of opposite handedness are distinguished by different colours. The right-handed segment is shown in green and cyan and the left-handed one in red and yellow. The dumbbell shown in purple and gray is the one switching from the right-handed segment to the left-handed one as the defect hops. The helical axis for the global minima is parallel to the static electric field, which is taken arbitrarily along the z-axis in the space-fixed frame. (Left) side-on view, (right) end-on view. Cooperative rotation of the two segments of opposite handedness in opposite directions is evident and reminiscent of the action of two gears working in tandem.

Supplementary Movie 2: Two representations of the pathway for the reversal of handedness for a supramolecular helix. The side-on view of the same pathway (left), as shown in Supplementary Movie 1, is shown along with a reduced representation (right), where only the position of the dipole vector and its direction are depicted for clarity. The right-handed segment is shown in green and the left-handed one in red. The dipole shown in purple corresponds to the dumbbell that is switching from the right-handed segment to the left-handed one as the defect hops. Periodic switching between an elongated and a compact state is evident in the reduced representation. It is also apparent from the movie how linear and rotary motion are coupled as the helix reverses handedness.

[1] D. Chakrabarti and D. J. Wales, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1970–1976.
[2] D. Chakrabarti, S. N. Fejer and D. J. Wales, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 20164–20167.
[3] D. J. Wales and J. P. K. Doye, *J. Phys. Chem. A*, 1997, **111**, 5111–5116.
[4] Z. Li and H. A. Scheraga, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 6611–6615.
[5] D. J. Wales, *Mol. Phys.*, 2002, **100**, 3285–3306.
[6] D. J. Wales, *Mol. Phys.*, 2004, **102**, 891–908.
[7] D. J. Wales, *Energy Landscapes*, Cambridge University Press, Cambridge, 2003.
[8] J. M. Carr and D. J. Wales, *J. Phys. Chem. B*, 2008, **112**, 8760–8769.
[9] C. Dellago, P. G. Bolhuis, F. S. Cśajka and D. Chandler, *J. Chem. Phys.*, 1998, **108**, 1964–1977.
[10] C. Dellago, P. G. Bolhuis and D. Chandler, *J. Chem. Phys.*, 1999, **110**, 6617–6625.
[11] P. G. Bolhuis, D. Chandler, C. Dellago and P. L. Geissler, *Annu. Rev. Phys. Chem.*, 2002, **53**, 291–318.

[12] S. A. Trygubenko and D. J. Wales, *J. Chem. Phys.*, 2004, **120**, 2082–2094.
[13] G. Henkelman and H. Jónsson, *J. Chem. Phys.*, 1999, **111**, 7010–7022.
[14] G. Henkelman and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9978–9985.
[15] G. Henkelman, B. P. Uberuaga. and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901–9904.
[16] J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 371–377.
[17] J. Nocedal, *Math. Comput.*, 1980, **35**, 773–782.
[18] D. Liu and J. Nocedal, *Mathematical Programming*, 1989, **45**, 503–528.
[19] D. A. Evans and D. J. Wales, *J. Chem. Phys.*, 2004, **121**, 1080–1090.
[20] E. W. Dijkstra, *Numerische Mathematlk*, 1959, **1**, 269–271.