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Electronic Supplementary Information for Assessment of an anisotropic coarse-grained model for cis-1,4-polybutadiene: a bottom-up approach

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S1. Expression for the effective torque

The equation

$$\frac{d\mathbf{I}(t)\boldsymbol{\omega}(t)}{dt} = \mathbf{T}(t), \tag{1}$$

is usually written down for rigid bodies with $\mathbf{T}(t)$ being the torque on the body with respect to its center of mass: $\mathbf{T} = \sum_{i\in\mu} \Delta\mathbf{r}_i \times \mathbf{f}_i$, where $\mathbf{f}_i$ is the force on atom i. Here as the body is not rigid this equality is not exactly true. However, the inertia tensor $\mathbf{I}$ and the vector $\boldsymbol{\omega}$ are well defined and their derivative can in principle be derived analytically and can obviously be computed numerically. By analogy to the case of a rigid body, we denote this derivative $\mathbf{T}(t)$ and name it the effective torque. In the current basis $(\mathbf{u}_1(t), \mathbf{u}_2(t), \mathbf{u}_3(t))$, the components of the angular velocity $\boldsymbol{\omega}(t)$ are $\boldsymbol{\omega}'(t)$ and those of vector $\mathbf{T}(t)$ are denoted $\mathbf{T}'(t)$. We have consequently:

$$\frac{d}{dt}\Big(\sum_{i=1}^{3} \omega_i'(t)\mathbf{I}(t)\mathbf{u}_i(t)\Big) = \sum_{i=1}^{3} T_i'(t)\mathbf{u}_i(t) \tag{2}$$

$$\frac{d}{dt}\Big(\sum_{i=1}^{3} \omega_i'(t)I_i(t)\mathbf{u}_i(t)\Big) = \sum_{i=1}^{3} T_i'(t)\mathbf{u}_i(t), \tag{3}$$

where $I_i(t)$ is the ith eigenvalue of the inertia tensor $\mathbf{I}(t)$, or the ith principal moment of inertia. We made use here of the fact that the basis vectors $(\mathbf{u}_1(t), \mathbf{u}_2(t), \mathbf{u}_3(t))$ are eigenvectors of $\mathbf{I}(t)$. Dropping the explicit time dependence and developing the

derivative with respect to time yields

$$\sum_{i=1}^{3} \dot{\omega}'_i I_i \mathbf{u}_i + \omega'_i \dot{I}_i \mathbf{u}_i + \omega'_i I_i \dot{\mathbf{u}}_i = \sum_{i=1}^{3} T'_i \mathbf{u}_i \tag{4}$$

$$\sum_{i=1}^{3} \dot{\omega}'_i I_i \mathbf{u}_i + \omega'_i \dot{I}_i \mathbf{u}_i + \omega'_i I_i (\boldsymbol{\omega} \times \mathbf{u}_i) = \sum_{i=1}^{3} T'_i \mathbf{u}_i. \tag{5}$$

In the current basis of eigenvectors $(\mathbf{u}_1(t), \mathbf{u}_2(t), \mathbf{u}_3(t))$, which is a direct orthonormal basis, the components of $\boldsymbol{\omega}$ are ω'_i, for $i \in 1, 2, 3$ and the component of $\mathbf{u}_i$ are trivial. It is then very easy to express the cross product $\boldsymbol{\omega} \times \mathbf{u}_i$ in the current basis. Collecting the three components in the current basis and reorganizing leads to

$$I_i \dot{\omega}'_i = T'_i - \dot{I}_i \omega'_i + \omega'_{i-1} \omega'_{i+1} (I_{i+1} - I_{i-1}), \tag{6}$$

with the convention that $i+1$ and $i-1$ are the indices following and preceding i in a circular permutation, respectively.

S2. Equation of motion for the quaternion

In this appendix, a quaternion is denoted with a sans serif character like Q, its components are denoted Q_0, Q_1, Q_2 and Q_3:

$$\mathsf{Q} = \begin{bmatrix} Q_0 \\ Q_1 \\ Q_2 \\ Q_3 \end{bmatrix}. \tag{7}$$

Q_0 is the scalar part of the quaternion and $(Q_1, Q_2, Q_3)^T$ forms a vector associated to the quaternion and denoted with a bold character $\mathbf{Q}$. We recall here the multiplication rule for two quaternions Q and Q' leading to a third quaternion $\mathsf{Q}'' = \mathsf{Q}\mathsf{Q}'$:

$$\begin{aligned} Q''_0 &= Q_0 Q'_0 - \mathbf{Q} \cdot \mathbf{Q}' \\ \mathbf{Q}'' &= Q_0 \mathbf{Q}' + Q'_0 \mathbf{Q} + \mathbf{Q} \times \mathbf{Q}', \end{aligned} \tag{8}$$

where $\cdot$ and $\times$ are the usual scalar and cross products applied to vectors, respectively. The conjugate of a quaternion Q is denoted Q^* and defined as

$$\begin{aligned} Q^*_0 &= Q_0 \\ \mathbf{Q}^* &= -\mathbf{Q} \end{aligned} \tag{9}$$

so that

$$\mathsf{Q}\mathsf{Q}^* = \mathsf{Q}^*\mathsf{Q} = \begin{bmatrix} \sum_{m=0}^{3} Q_m^2 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{10}$$

To obtain the equation of motion for the quaternion Q_μ, we follow closely the proof done for rigid bodies in Ref. [1]. The main difference is that the proof is applied to the eigenvectors of the inertia tensor instead of being applied to any atomic position respectively to the center of mass of the rigid body. In the following the index μ is dropped for clarity. We use the rotation matrix $\mathbf{C}(t)$ defined as transforming the current basis of eigenvectors $(\mathbf{u}_1(t), \mathbf{u}_2(t), \mathbf{u}_3(t))$ back into the reference basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ in terms of the quaternion Q_μ:

$$\mathbf{e}_i = \mathbf{C}(t)\mathbf{u}_i(t), \forall i \in \{1, 2, 3\}. \tag{11}$$

Equation 11 is equivalent to

$$\mathsf{u}_i(t) = \mathsf{Q}(t)\mathsf{e}_i\mathsf{Q}(t)^*, \tag{12}$$

where the quaternion $\mathsf{u}_i(t)$ associated to the eigenvector $\mathbf{u}_i(t)$ is defined as

$$\mathsf{u}_i(t) = \begin{bmatrix} 0 \\ u_{i,1}(t) \\ u_{i,2}(t) \\ u_{i,3}(t) \end{bmatrix}. \tag{13}$$

Differentiating Eq. 12 with respect to time yields

$$\begin{aligned}
\dot{\mathsf{u}}_i(t) &= \dot{\mathsf{Q}}(t)\mathsf{u}_i(0)\mathsf{Q}(t)^* + \mathsf{Q}(t)\mathsf{u}_i(0)\dot{\mathsf{Q}}(t)^* && (14)\\
&= \dot{\mathsf{Q}}(t)\mathsf{Q}(t)^*\mathsf{Q}(t)\mathsf{e}_i\mathsf{Q}(t)^* + \mathsf{Q}(t)\mathsf{e}_i\mathsf{Q}(t)^*\mathsf{Q}(t)\dot{\mathsf{Q}}(t)^* \quad \text{because } \mathsf{Q}\mathsf{Q}^* = \mathsf{1}, && (15)\\
&= \dot{\mathsf{Q}}(t)\mathsf{Q}(t)^*\mathsf{u}_i(t) + \mathsf{u}_i(t)\mathsf{Q}(t)\dot{\mathsf{Q}}(t)^* \quad \text{through Eq. 12 ,} && (16)\\
&= \dot{\mathsf{Q}}(t)\mathsf{Q}(t)^*\mathsf{u}_i(t) - \mathsf{u}_i(t)\dot{\mathsf{Q}}(t)\mathsf{Q}(t)^* \quad \text{because } \mathsf{Q}\dot{\mathsf{Q}}^* = \dot{\mathsf{1}} = \mathsf{0}. && (17)
\end{aligned}$$

We define

$$\mathsf{g}(t) = \dot{\mathsf{Q}}(t)\mathsf{Q}(t)^* \tag{18}$$

hence

$$\dot{\mathsf{u}}_i(t) = \mathsf{g}(t)\mathsf{u}_i(t) - \mathsf{u}_i(t)\mathsf{g}(t). \tag{19}$$

The scalar part of $\dot{\mathsf{u}}_i(t)$ is zero by definition because $\dot{\mathbf{u}}_i(t)$ is a pure vector. The vector part of $\dot{\mathsf{u}}_i(t)$ is, using the multiplication rule for quaternion,

$$\begin{aligned}
\dot{\mathbf{u}}_i(t) &= \mathbf{g}(t) \times \mathbf{u}_i(t) - \mathbf{u}_i(t) \times \mathbf{g}(t) && (20)\\
&= 2\mathbf{g}(t) \times \mathbf{u}_i(t). && (21)
\end{aligned}$$

Moreover, for the three eigenvectors $\mathbf{u}_i(t)$, $i = 1, 2, 3$, one can define a unique angular velocity $\boldsymbol{\omega}(t)$ such that

$$\dot{\mathbf{u}}_i(t) = \boldsymbol{\omega}(t) \times \mathbf{u}_i(t). \tag{22}$$

One can see immediately that this angular velocity is related to the quaternion $\mathsf{g}(t)$ through

$$\begin{aligned}
\boldsymbol{\omega}(t) &= 2\mathbf{g}(t) && (23)\\
&= 2(-\dot{Q}_0\mathbf{Q} + Q_0\dot{\mathbf{Q}} - \dot{\mathbf{Q}} \times \mathbf{Q}), && (24)
\end{aligned}$$

where the time dependence is made implicit. The components of all vectors and matrices defined until now can be expressed in any basis. For the sake of simplicity, the components of the vector $\boldsymbol{\omega}(t)$ in the reference basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ are denoted with the same letter $\boldsymbol{\omega}(t)$ and its components in the current basis $(\mathbf{u}_1(t), \mathbf{u}_2(t), \mathbf{u}_3(t))$ are denoted $\boldsymbol{\omega}'(t)$. It is useful to define $\boldsymbol{\omega}'(t)$ because the equation of motion of the atoms inside bead μ are much easier to write down in the current basis, where the inertia tensor is diagonal. The two sets of components $\boldsymbol{\omega}'$ and $\boldsymbol{\omega}$ can also be seen as two different vectors related by

$$\boldsymbol{\omega}'(t) = \mathbf{C}(t)\boldsymbol{\omega}(t), \tag{25}$$

where $\mathbf{C}(t)$ is again the rotation matrix. The corresponding quaternion $\mathsf{g}'(t)$ is defined as

$$\begin{aligned} \mathsf{g}'(t) &= \mathsf{Q}(t)^*\mathsf{g}(t)\mathsf{Q}(t), & (26)\\ &= \mathsf{Q}(t)^*\dot{\mathsf{Q}}(t)\mathsf{Q}(t)^*\mathsf{Q}(t) & (27)\\ &= \mathsf{Q}(t)^*\dot{\mathsf{Q}}(t) & (28) \end{aligned}$$

and

$$\boldsymbol{\omega}'(t) = 2\mathbf{g}'(t). \tag{29}$$

Using the multiplication rule, Eq. 29 develops to

$$\boldsymbol{\omega}'(t) = 2(Q_0\dot{\mathbf{Q}} - \dot{Q}_0\mathbf{Q} - \mathbf{Q}\times\dot{\mathbf{Q}}), \tag{30}$$

or in matrix form

$$\dot{\mathsf{Q}} = \frac{1}{2}\mathbf{A}\mathsf{w}'(t) \tag{31}$$

where matrix $\mathbf{A}$ is

$$\mathbf{A} = \begin{bmatrix} Q_0 & -Q_1 & -Q_2 & -Q_3 \\ Q_1 & Q_0 & -Q_3 & Q_2 \\ Q_2 & Q_3 & Q_0 & -Q_1 \\ Q_3 & -Q_2 & Q_1 & Q_0 \end{bmatrix}. \tag{32}$$

Eq. 31 is the equation of motion for the quaternion. Note that this equation can be used as a practical way to obtain the angular velocity $\boldsymbol{\omega}'(t)$ in the current basis from the derivative of the quaternion, as the inverse of matrix $\mathbf{A}$ is its transpose.

To obtain the equation of motion for $\dot{\mathsf{Q}}(t)$, we derive Eq. 28:

$$\dot{\mathsf{g}'} = \dot{\mathsf{Q}}^*\dot{\mathsf{Q}} + \mathsf{Q}^*\ddot{\mathsf{Q}}. \tag{33}$$

Multiplying on the left hand side by Q yields

$$\begin{aligned} \mathsf{Q}\dot{\mathsf{g}'} &= \mathsf{Q}\dot{\mathsf{Q}}^*\dot{\mathsf{Q}} + \ddot{\mathsf{Q}} & (34)\\ \ddot{\mathsf{Q}} &= \mathsf{Q}\dot{\mathsf{g}'} - \mathsf{Q}\dot{\mathsf{Q}}^*\dot{\mathsf{Q}}. & (35) \end{aligned}$$

Reformulating the first term of the sum on the right hand-side of Eq. 35 using Eq. 29 leads to

$$\mathsf{Q}\dot{\mathsf{g}}' = \begin{bmatrix} -\frac{1}{2}\sum_{m=0}^{3} Q_m \dot{\omega}'_m \\ \frac{1}{2}Q_0\dot{\omega}'_1 + \frac{1}{2}(Q_2\dot{\omega}'_3 - Q_3\dot{\omega}'_2) \\ \frac{1}{2}Q_0\dot{\omega}'_2 + \frac{1}{2}(Q_3\dot{\omega}'_1 - Q_1\dot{\omega}'_3) \\ \frac{1}{2}Q_0\dot{\omega}'_3 + \frac{1}{2}(Q_1\dot{\omega}'_2 - Q_2\dot{\omega}'_1) \end{bmatrix} \tag{36}$$

Moreover, in the second term of the sum on the right hand side of Eq. 35 the quaternion $\mathsf{Q}\dot{\mathsf{Q}}^*\dot{\mathsf{Q}}$, has only a scalar part equals to $\sum_m \dot{Q}_m^2$, so that

$$\mathsf{Q}\dot{\mathsf{Q}}^*\dot{\mathsf{Q}} = (\sum_{m=0}^{3} \dot{Q}_m^2)\mathsf{Q}. \tag{37}$$

Introducing the result of Eqs. 36 and 37 into Eq. 35 leads in matrix form to

$$\begin{bmatrix} \ddot{Q}_0 \\ \ddot{Q}_1 \\ \ddot{Q}_2 \\ \ddot{Q}_3 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} Q_0 & -Q_1 & -Q_2 & -Q_3 \\ Q_1 & Q_0 & -Q_3 & Q_2 \\ Q_2 & Q_3 & Q_0 & -Q_1 \\ Q_3 & -Q_2 & Q_1 & Q_0 \end{bmatrix} \begin{bmatrix} -2\sum_{m=0}^{3} \dot{Q}_m^2 \\ \dot{\omega}'_1 \\ \dot{\omega}'_2 \\ \dot{\omega}'_3 \end{bmatrix}, \tag{38}$$

where matrix $\mathbf{A}$ can be recognized. Note again that Eq. 38 can be used to obtain the time derivative of the angular velocity $\dot{\boldsymbol{\omega}}'$ from the second derivative of the quaternion.

S3. Computation of the average force and effective torque

The average pair force $\langle \mathbf{F}_{\mu\nu} \rangle$ and the average pair effective torque $\langle \mathbf{T}_{\mu\nu} \rangle$ are needed to estimate the coarse-grained potential. The average pair force $\langle \mathbf{F}_{\mu\nu} \rangle$ is estimated in the following way. We assume that

$$\langle \mathbf{F}_{\mu\nu} \rangle = \frac{1}{2}\langle (\mathbf{F}_\mu - \mathbf{F}_\nu) \rangle. \tag{39}$$

This is exactly true if there are only pair interactions at the atomic level and when the average is done for all atomic variables and not only for the fast ones. It has been checked in Ref. [2] for alkanes that doing the average on all variables does not change the result. As $\mathbf{e}_{\mu\nu}$ depends only on the slow variables it can be included in the average and one finally gets

$$\frac{\partial W}{\partial R_{\mu\nu}}(R_{\mu\nu}, \cos\phi_{\mu\nu}) = -\frac{1}{2}\langle (\mathbf{F}_\mu - \mathbf{F}_\nu) \cdot \mathbf{e}_{\mu\nu} \rangle_{(R,\phi)}, \tag{40}$$

where the dependence of the average $\langle \cdot \rangle$ on $R_{\mu\nu}$ and $\phi_{\mu\nu}$ only and not on all the slow variables has been highlighted. Eq. 40 can be directly used to compute the derivative of the potential with respect to the distance using molecular dynamics simulations where the force on each bead is known exactly and in which the average can be

computed. Moreover, the derivative $\partial W/\partial R_{\mu\nu}$ is an even function of $\cos\phi_{\mu\nu}$. Indeed, the two configurations where the orientations of beads μ and ν are characterized by $(\mathbf{u}_{\mu,1}, \mathbf{u}_{\nu,1})$ and $(\mathbf{u}_{\mu,1}, -\mathbf{u}_{\nu,1})$ are identical and should lead to the same force between the two beads, whereas they lead to two opposite values of $\cos\phi_{\mu\nu}$. The fact that $\partial W/\partial R_{\mu\nu}$ is an even function of $\cos\phi_{\mu\nu}$ was checked within numerical noise (not shown) and to optimize the statistics, $\partial W/\partial R_{\mu\nu}$ is only computed for $\cos\phi_{\mu\nu} \in [0,1]$ using all possible values of $\cos\phi_{\mu\nu}$.

For the average pair effective torque, we assume similarly that

$$\langle \mathbf{T}_{\mu\nu} \rangle = \frac{1}{2}\langle (\mathbf{T}_\mu - \mathbf{T}_\nu) \rangle, \tag{41}$$

and get

$$\frac{\partial W}{\partial \cos\phi_{\mu\nu}} = -\frac{1}{2\sin^2\phi_{\mu\nu}} \langle (\mathbf{T}_\mu - \mathbf{T}_\nu) \cdot (\mathbf{u}_{\mu,1} \times \mathbf{u}_{\nu,1}) \rangle_{R,\phi}. \tag{42}$$

This cannot yet be used directly in molecular dynamics simulations because $\mathbf{T}_\mu$ is the effective torque. Its expression in terms of atomic variables is given in the current basis in Eq. 6, involving the angular velocity $\boldsymbol{\omega}'$, its derivative $\dot{\boldsymbol{\omega}}'$, the moments of inertia I_i and their derivatives. These quantities can be calculated from molecular dynamics knowing the positions of all atoms for three consecutive time steps along a long trajectory. The moments of inertia of each bead are directly computed as the eigenvalues of the inertia tensor. Their derivatives are computed as $\dot{I} = (I(t+dt) - I(t))/dt$, where $I(t+dt)$ is the same moment of inertia of the same bead at time $t+dt$ and dt is the time step. The angular velocity $\boldsymbol{\omega}'$ and its derivative $\dot{\boldsymbol{\omega}}'$ are computed using Eqs 31 and 38, respectively. This implies to compute the quaternions of all beads and their first and second derivatives with respect to time. Some care needs to be taken to guarantee that the same basis of eigenvalues between the few equivalent ones is chosen for times t, $t+dt$, and $t+2dt$ as noted by Kempfer et al [3], and that the same quaternion and not its opposite is computed, see ESI, Sec. S6, for details. After all these calculations, one can get the effective torque on each bead for many configurations. Equation 42 can then be used to get $\partial W/\partial\cos\phi_{\mu\nu}$. Moreover, Eq. 42 induces that the derivative $\partial W/\partial\cos\phi_{\mu\nu}$ is an odd function of $\cos\phi_{\mu\nu}$: the torque between bead μ and ν is identical whether $\mathbf{u}_{\nu,1}$ or $-\mathbf{u}_{\nu,1}$ is considered whereas the cross product $\mathbf{u}_{\mu,1} \times \mathbf{u}_{\nu,1}$ changes sign. As for the force, this was checked (not shown) and $\partial W/\partial R_{\mu\nu}$ is only computed for $\cos\phi_{\mu\nu} \in [0,1]$ using all possible values of $\cos\phi_{\mu\nu}$.

S4. Smoothing procedure

The raw potential is smoothed within empirically chosen bounds and extended to a continuous and differentiable function beyond the bounds. This procedure is useful to get a smoother potential and consequently a smoother force and torque. The bounds are necessary to eliminate from the smoothing procedure regions of phase space where the noise is high.

The smoothing and extension procedures are illustrated in Fig. 1. The smoothing is done using a Savitzky-Golay filter [4, 5] first as a function of the distance $R_{\mu\nu}$

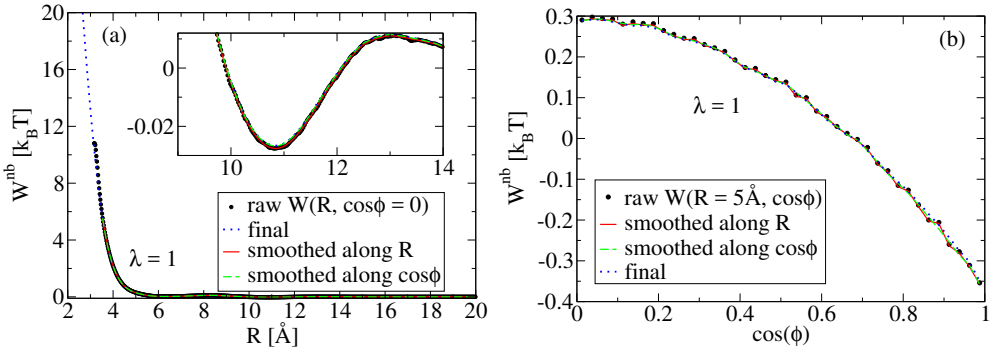

Figure 1: (a) Variation of the non-bonded potential $W^{\rm nb}$ with the distance R for $\cos\phi = 0$ for a level of coarse-graining λ of 1 monomer per bead. The black circles correspond to the raw data, after integration. The red solid line corresponds to the data after the smoothing procedure along R has been applied for $R > 3.5$ Å. The dashed green line corresponds to the data after both smoothing procedures have been applied. The blue dotted line correspond to the final potential, after the smoothing and extension procedure have been applied. (b) Same as (a) for the variation with $\cos\phi$ at $R = 5$Å.

for all values of $\cos\phi_{\mu\nu}$ within bounds which depend on $\cos\phi_{\mu\nu}$. Then, the result is smoothed as a function of $\cos\phi_{\mu\nu}$ for all values of $R_{\mu\nu}$ within bounds deduced from the first bounds given. The effect of the smoothing procedures are shown as a function of $R_{\mu\nu}$ in Fig. 1 (a) and as a function of $\cos\phi_{\mu\nu}$ in Fig. 1 (b) for a level of coarse-graining λ of 1 monomer per bead. As expected, the smoothing procedure along $R_{\mu\nu}$ is more convincing for the potential plotted against $R_{\mu\nu}$ and the smoothing procedure along $\cos\phi_{\mu\nu}$ is more convincing for the potential plotted against $\cos\phi_{\mu\nu}$. Fortunately, after both smoothing procedures are performed the final smoothed potential is quite similar to the potential smoothed along $R_{\mu\nu}$ only and still corresponds very well to the raw data plotted against $R_{\mu\nu}$ as can be seen in the inset of Fig. 1 (a). Meanwhile, the smoothness against $\cos\phi_{\mu\nu}$ is improved after the smoothing procedure along this variable as can be seen in Fig. 1 (b). For these two reasons, we considered our simple smoothing procedure in two steps as good enough for our purpose. After the smoothing procedures are performed, the zero of the potential is recalculated at the cutoff distance $R_{\mu\nu} = R_c$ and $\cos\phi_{\mu\nu} = 0$ for non-bonding interactions.

Finally, the smoothed function is extended to a continuous and differentiable function of $R_{\mu\nu}$ for all values of $\cos\phi_{\mu\nu}$ beyond the first bounds given. An example of the final potential and its extension is displayed in Fig. 1 (a). In the inset of this figure, one can see a small difference between the final extended potential and the smoothed potential around 11Å. This is due to the recalculation of the zero of the potential for $R = R_c$ and $\cos\phi = 0$ between the smoothing and extension procedures. The effect is extremely small. To conclude on the smoothing procedures, the effect is the one expected: a smoother function of both $R_{\mu\nu}$ and $\cos\phi_{\mu\nu}$ still very close to the raw data.

S5. An intramolecular 1,3 anisotropic pair potential

In order to stay strictly within the pair approximation, we derived an intramolecular 1,3 potential $W^{\mathrm{intra1,3}}$ depending on the distance between beads 1 and 3 and the angle between their relative orientations. It is shown in Figs. 2 (a) and (b) for a level of coarse-graining λ of 1 monomer per bead. The minimum of the intramolecular 1,3 potential plotted against R is quite flat and is shifted from the interval [4 Å−8 Å] to [5 Å−9 Å] as $\cos\phi$ increases. The corresponding intramolecular 1,3 isotropic potential has an even larger minimum between $R = 4$ Å and $R = 9$ Å. As for the bonding potential, the effect of the orientation on the intramolecular 1,3 potential is important: at a distance of 9 Å, the potential varies of nearly 20 k_BT between $\cos\phi = 0$ and $\cos\phi = 1$

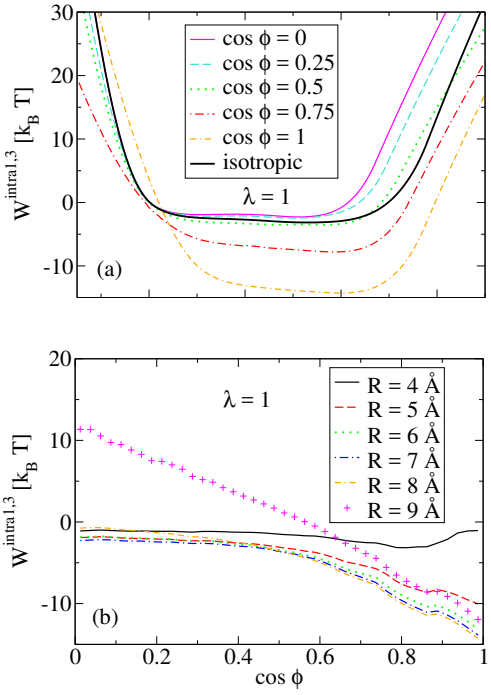

Figure 2: (a) Variation of the intramolecular 1,3 potential $W^{\mathrm{intra1,3}}$ with the distance R for different values of $\cos\phi$ for a level of coarse-graining λ of 1 monomer per bead. The thick black lines correspond to the isotropic potential. The results are shown after the smoothing and extension procedures have been applied. (b) Same as (a) for the variation with $\cos\phi$ at different values of R.

S6. Choosing the same basis and the same quaternion at two consecutive time steps

To compute the angular velocity and the effective torque on each bead in the current basis, we need to compute the first and second derivative of the quaternion of each bead. To get these numerically, we need to determine the same quaternion at times t, $t + dt$, and $t + 2dt$, where dt is the MD time step. This appendix explains how to get the same quaternion at times t and $t + dt$, the exact same procedure can be applied to get the same quaternion at times $t + dt$ and $t + 2dt$.

The quaternion at each time step is calculated from the rotation matrix whose components are in column the eigenvectors $\mathbf{u}_1(t)$, $\mathbf{u}_2(t)$, and $\mathbf{u}_3(t)$ of the inertia tensor of each bead using a standard method [6], detailed in the website `https://www.euclideanspace.com/maths/geometry/rotations/conversions/matrixToQuaternion/`.

First, we need to choose a unique combination of the eigenvectors $\mathbf{u}_1(t)$, $\mathbf{u}_2(t)$, and $\mathbf{u}_3(t)$ at time t. As the inertia tensor is a symmetric matrix, its eigenvectors form an orthonormal basis. The eigenvectors can be sorted from the lowest corresponding eigenvalue to the highest. We choose a direct orthonormal basis among all the orthonormal bases possible, by changing the sign of one of the eigenvectors if necessary. There are four equivalent direct orthonormal bases of sorted eigenvectors: $(\mathbf{u}_1(t), \mathbf{u}_2(t), \mathbf{u}_3(t))$, $(-\mathbf{u}_1(t), -\mathbf{u}_2(t), \mathbf{u}_3(t))$, $(-\mathbf{u}_1(t), \mathbf{u}_2(t), -\mathbf{u}_3(t))$, $(\mathbf{u}_1(t), -\mathbf{u}_2(t), -\mathbf{u}_3(t))$. We choose one of them arbitrarily.

The second thing to secure is that the same eigenvectors at time t and $t + dt$ are calculated. The first possible change between times t and $t + dt$ is a change in the numerical order of the eigenvalues. It is especially possible for the two highest eigenvalues which are close. To prevent any such exchange between the sorted eigenvectors, we keep the order chosen at time t, by checking that in absolute value $|\mathbf{u}_1(t)\cdot\mathbf{u}_1(t+dt)| > |\mathbf{u}_1(t)\cdot\mathbf{u}_2(t+dt)|$ and $|\mathbf{u}_1(t)\cdot\mathbf{u}_1(t+dt)| > |\mathbf{u}_1(t)\cdot\mathbf{u}_3(t+dt)|$. If it is not the case and if $|\mathbf{u}_1(t)\cdot\mathbf{u}_1(t+dt)| < |\mathbf{u}_1(t)\cdot\mathbf{u}_2(t+dt)|$, we check first that $\mathbf{u}_3(t+dt)$ is not to be changed by verifying that $|\mathbf{u}_3(t)\cdot\mathbf{u}_3(t+dt)| > |\mathbf{u}_1(t)\cdot\mathbf{u}_3(t+dt)|$, and then exchange $\mathbf{u}_1(t+dt)$ and $\mathbf{u}_2(t+dt)$. If instead $|\mathbf{u}_1(t)\cdot\mathbf{u}_1(t+dt)| < |\mathbf{u}_1(t)\cdot\mathbf{u}_3(t+dt)|$, we do the same with $\mathbf{u}_1(t+dt)$ and $\mathbf{u}_3(t+dt)$. Finally if $\mathbf{u}_1(t+dt)$ does not need to be swapped with either $\mathbf{u}_2(t+dt)$ or $\mathbf{u}_3(t+dt)$, we check that $|\mathbf{u}_2(t)\cdot\mathbf{u}_2(t+dt)| > |\mathbf{u}_2(t)\cdot\mathbf{u}_3(t+dt)|$. If not, the exchange between $\mathbf{u}_2(t+dt)$ and $\mathbf{u}_3(t+dt)$ is done. This guarantees that the eigenvectors are in the same order at time t and $t + dt$. A case, where the exchange between the eigenvectors was undetermined was never encountered. The second possible change for the eigenvectors is their sign. After the order has been secured, we consequently check the sign of $\mathbf{u}_i(t)\cdot\mathbf{u}_i(t+dt)$, for all $i \in 1, 2, 3$ and change the sign of $\mathbf{u}_i(t+dt)$ if the dot product is negative. We now have the exact same basis of eigenvectors. The smoothness of the change can be checked on the autocorrelation function of each eigenvector displayed in Fig. 5.

The last thing to secure is that the same quaternion is obtained from the rotation matrix. The only thing left undetermined is the sign of the quaternion itself, because the rotations of π and $-\pi$ around the same axis yield the same rotation matrix but two opposite quaternions. If $Q_0(t)Q_0(t+dt) + Q_1(t)Q_1(t+dt) + Q_2(t)Q_2(t+dt) +$

$Q_3(t)Q_3(t+dt) < -0.99$ we change the sign of $\mathsf{Q}(t+dt)$. After all this is done, there is no abrupt change in the quaternion components or unphysical large value of $\dot{\mathsf{Q}}$. The numerical evaluation of the angular velocity, the effective torque and also of the quantity $\boldsymbol{\epsilon}$ associated to the time derivative of the moments of inertia is always done after all this procedure is completed.

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