Supporting Information for Molecular Dynamics simulations of energy dissipation on amorphous solid water: testing the validity of equipartition

Adrien Fredon,[†] Gerrit C. Groenenboom,[†] and Herma M. Cuppen[*,†,‡]

†*Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands.*

‡*van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands*

E-mail: h.cuppen@science.ru.nl

1 Sampling the rotational motion of a nonlinear molecule

The ensemble average of an observable $A(\boldsymbol{q},\boldsymbol{p})$ is given by an average over phase space,[1]

$$\langle A\rangle = \frac{\int\cdots\int A(\boldsymbol{q},\boldsymbol{p})\rho(\boldsymbol{q},\boldsymbol{p})\,d\boldsymbol{q}\,d\boldsymbol{p}}{\int\cdots\int \rho(\boldsymbol{q},\boldsymbol{p})\,d\boldsymbol{q}\,d\boldsymbol{p}}, \tag{1}$$

where $\boldsymbol{q}$ is the vector with the coordinates of the configuration space and $\boldsymbol{p}$ is the vector of momenta conjugate to these coordinates. The density of states $\rho(\boldsymbol{q},\boldsymbol{p})$ for a microcanonical ensemble is given by

$$\rho(\boldsymbol{q},\boldsymbol{p}) = \delta[E - H(\boldsymbol{q},\boldsymbol{p})], \tag{2}$$

where δ is the Dirac delta-function, E is the total energy, and $H(\boldsymbol{q},\boldsymbol{p})$ is the Hamiltonian of the system. For a nonlinear rotor, the configuration space coordinates are the zyz-Euler

angles

$$\boldsymbol{q} = \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}, \tag{3}$$

which define the Cartesian coordinates of the atoms $\boldsymbol{r}_i$ through a rotation,

$$\boldsymbol{r}_i = \boldsymbol{R}(\boldsymbol{q})\boldsymbol{r}_i^{(0)}, \quad \text{for } i = 1, 2, \ldots, N, \tag{4}$$

where N is the number of atoms and $\boldsymbol{r}_i^{(0)}$ are the Cartesian coordinates of the atoms for the reference geometry in a center-of-mass frame. The zyz-Euler rotation matrix is given by

$$\boldsymbol{R}(\boldsymbol{q}) = \boldsymbol{R}_z(\alpha)\boldsymbol{R}_y(\beta)\boldsymbol{R}_z(\gamma) \tag{5}$$

with

$$\boldsymbol{R}_z(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{6}$$

and

$$\boldsymbol{R}_y(\beta) = \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{pmatrix}. \tag{7}$$

The velocities of the atoms are related to the time-derivative of the rotation matrix,

$$\dot{\boldsymbol{r}}_i = \dot{\boldsymbol{R}}(\boldsymbol{q})\boldsymbol{r}_i^{(0)} = \dot{\boldsymbol{R}}(\boldsymbol{q})\boldsymbol{R}(\boldsymbol{q})^T\boldsymbol{r}_i = \boldsymbol{\Omega}\boldsymbol{r}_i. \tag{8}$$

The matrix $\boldsymbol{\Omega}$ is antisymmetric, which can be shown by taking the time derivative of the relation $\boldsymbol{R}(\boldsymbol{q})^T\boldsymbol{R}(\boldsymbol{q}) = \mathbb{1}_{3\times3}$, and hence the matrix-vector product $\boldsymbol{\Omega}\boldsymbol{r}$ can be written as a

cross product,

$$\boldsymbol{\Omega r} = \begin{pmatrix} 0 & -\omega_z & \omega_y \\ \omega_z & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{pmatrix} \boldsymbol{r} = \boldsymbol{\omega} \times \boldsymbol{r}, \tag{9}$$

where $\boldsymbol{\omega}$ is the vector with components ω_x, ω_y, and ω_z. This vector is related to the time derivatives of the Euler angles: from the relation

$$\dot{\boldsymbol{r}}_i = \frac{\partial}{\partial t}\boldsymbol{R}(\boldsymbol{q})\boldsymbol{r}_i^{(0)} = \sum_{j=1}^{3} \dot{q}_j \left[\frac{\partial \boldsymbol{R}(\boldsymbol{q})}{\partial q_j}\right] \boldsymbol{R}^T(\boldsymbol{q})\boldsymbol{r}_i = \boldsymbol{\Omega r}_i \tag{10}$$

we find

$$\boldsymbol{\omega} = \boldsymbol{M}\dot{\boldsymbol{q}} \tag{11}$$

with

$$\boldsymbol{M} = \begin{pmatrix} 0 & -\sin\alpha & \cos\alpha \sin\beta \\ 0 & \cos\alpha & \sin\alpha \sin\beta \\ 1 & 0 & \cos\beta \end{pmatrix}. \tag{12}$$

The total angular momentum of the molecule is

$$\boldsymbol{L} = \sum_{i=1}^{M} \boldsymbol{r}_i \times \boldsymbol{P}_i = \sum_{i=1}^{M} m_i\, \boldsymbol{r}_i \times \dot{\boldsymbol{r}}_i = \sum_{i=1}^{M} m_i\, \boldsymbol{r}_i \times (\boldsymbol{\omega} \times \boldsymbol{r}_i) = \boldsymbol{I}\boldsymbol{\omega}, \tag{13}$$

where $\boldsymbol{P}_i = m_i \dot{\boldsymbol{r}}_i$ are the Cartesian linear momenta and the inertia tensor is given by

$$\boldsymbol{I} = \sum_{i=1}^{N} m_i \left[(\boldsymbol{r}_i^T \boldsymbol{r}_i)\mathbb{1}_{3\times 3} - \boldsymbol{r}_i \boldsymbol{r}_i^T\right]. \tag{14}$$

The rotational Hamiltonian is

$$H = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \cdot \dot{\boldsymbol{r}}_i = \frac{1}{2}\sum_{i=1}^{N} m_i (\boldsymbol{\omega} \times \boldsymbol{r}_i) \cdot (\boldsymbol{\omega} \times \boldsymbol{r}_i) = \frac{1}{2}\boldsymbol{\omega}^T \boldsymbol{I}\boldsymbol{\omega}. \tag{15}$$

To find the momenta conjugate to the Euler angles ($\boldsymbol{q}$) we first express the Hamiltonian in terms of the velocities $\dot{\boldsymbol{q}}$ using Eq. (11):

$$H(\boldsymbol{q}, \dot{\boldsymbol{q}}) = \frac{1}{2} \dot{\boldsymbol{q}}^T \boldsymbol{M}^T \boldsymbol{I} \boldsymbol{M} \dot{\boldsymbol{q}}. \tag{16}$$

The momenta conjugate to the Euler angles are

$$p_i = \frac{\partial}{\partial \dot{q}_i} H(\boldsymbol{q}, \dot{\boldsymbol{q}}), \tag{17}$$

which gives

$$\boldsymbol{p} = \boldsymbol{M}^T \boldsymbol{I} \boldsymbol{M} \dot{\boldsymbol{q}} = \boldsymbol{M}^T \boldsymbol{I} \boldsymbol{\omega} = \boldsymbol{M}^T \boldsymbol{L}. \tag{18}$$

With the notation $p_\alpha = p_1$, $p_\beta = p_2$, and $p_\gamma = p_3$, the volume element for integration over phase space is[2]

$$d\tau = h^{-3} d\alpha \, d\beta \, d\gamma \, dp_\alpha \, dp_\beta \, dp_\gamma = h^{-3} d\alpha \, \sin\beta \, d\beta \, d\gamma \, dL_x \, dL_y \, dL_z, \tag{19}$$

where $\sin\beta = |\det(M)|$ is the Jacobian of the transformation from the momenta conjugate to the Euler angles ($\boldsymbol{p}$) to the angular momenta $\boldsymbol{L}$. The factor h^{-3}, with h Planck's constant, cancels when calculating an expectation value of an observable, so it is not important here. The ranges for Euler angles α and γ are $[0, 2\pi]$ and the range of β is $[0, \pi]$. The volume element for integration over configuration space is $d\alpha \, \sin\beta d\beta, d\gamma$, so averaging over the momenta for a given orientation only requires the volume element $dL_x \, dL_y \, dL_z$.

To express the Hamiltonian in angular momenta we combine Eqs. (13) and (15),

$$H = \frac{1}{2} \boldsymbol{L}^T \boldsymbol{I}^{-1} \boldsymbol{L}. \tag{20}$$

The principle axis frame

$$\boldsymbol{U} = [\boldsymbol{u}_x \, \boldsymbol{u}_y \, \boldsymbol{u}_z] \tag{21}$$

and moments of inertia I_x, I_y, and I_z are found by solving the eigenvalue problem

$$\boldsymbol{I}\boldsymbol{u}_i = I_i \boldsymbol{u}_i, \quad \text{for } i = x, y, z. \tag{22}$$

With the angular momenta in the principle axes frame $\widetilde{\boldsymbol{L}}$ defined by

$$\boldsymbol{L} = \boldsymbol{U}\widetilde{\boldsymbol{L}}, \tag{23}$$

the Hamiltonian becomes

$$\mathcal{H} = \frac{1}{2}\left(\frac{\widetilde{L}_x^2}{I_x} + \frac{\widetilde{L}_y^2}{I_y} + \frac{\widetilde{L}_z^2}{I_z}\right). \tag{24}$$

Since the transformation between space-fixed and principle-axes frame angular momenta is unitary, the momenta part $d\tau$ of the phase space volume element is

$$d\widetilde{\tau} = d\widetilde{L}_x \, d\widetilde{L}_y \, d\widetilde{L}_z. \tag{25}$$

To generate a microcanonical ensemble of the angular momenta in the principle-axes frame it is convenient to introduce the spherical polar coordinates θ and ϕ through

$$\widetilde{L}_x = \sqrt{2I_x E'} \, \cos\phi \, \sin\theta \tag{26}$$

$$\widetilde{L}_y = \sqrt{2I_y E'} \, \sin\phi \, \sin\theta \tag{27}$$

$$\widetilde{L}_z = \sqrt{2I_z E'} \, \cos\theta, \tag{28}$$

which gives $\mathcal{H} = E'$. The volume element in these coordinates

$$d\widetilde{\tau} = \sqrt{8I_x I_y I_z E'^3} \, dE' \sin\theta \, d\theta \, d\phi = \sqrt{8I_x I_y I_z E'^3} \, dE' dz \, d\phi, \tag{29}$$

where $z \equiv \cos\theta$ and $z \in [-1, 1]$. This volume element corresponds to a uniform distribution on a sphere. When calculating an ensemble averages, the integral over E' gives $E = E'$

because of the Dirac delta function [Eq. (2)].

Thus, to generate initial velocities of the atoms that correspond to a microcanonical ensemble of a nonlinear rotor, we generate pairs of z and ϕ, with z from a uniform distribution in the interval $[-1, 1]$ and ϕ from a uniform distribution in the interval $[0, 2\pi]$. We find the principle axes-frame angular momenta from Eqs. (26)-(28), with $E' = E$. They are transformed to the space-fixed angular moment with Eq. (23) and with $\boldsymbol{\omega} = \boldsymbol{I}^{-1}\boldsymbol{L}$ we get the atomic velocities from Eq. (10) as $\dot{\boldsymbol{r}}_i = \boldsymbol{\omega} \times \boldsymbol{r}_i$. For linear molecules the procedure is simpler, since we only have to consider the angular momenta $\widetilde{L}_x$ and $\widetilde{L}_y$, which are perpendicular to the interatomic axis, and no diagonalization is needed to find the principle axis frame and moments of inertia $\widetilde{I}_x = \widetilde{I}_y$.

References

(1) McQuarrie, D. A. *Statistical Mechanics*; Harper and Row: New York, 1976.

(2) Desloge, E. A. Classical partition function of a rigid rotator. *Am. J. Phys.* **1984**, *52*, 261–262.