**Supplementary material:**

Computing spatially resolved rotational hydration entropies from atomistic simulations

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Derivation of the test-distribution entropies

We describe elements of $SO(3)$ using quaternions that are, if treated as vectors, also elements of the 3-sphere by design. To carry out the integrations, it is therefore convenient to use the appropriate spherical coordinates:

\[ q_1 = \cos \phi_1, \]
\[ q_2 = \sin \phi_1 \cos \phi_2, \]
\[ q_3 = \sin \phi_1 \sin \phi_2 \cos \phi_3, \]
\[ q_4 = \sin \phi_1 \sin \phi_2 \sin \phi_3, \]

with $\phi_1 \in [0, \pi/2)$, $\phi_2 \in [0, \pi)$, $\phi_2 \in [0, 2\pi)$. Because, for quaternions, $q$ and $-q$ denote the same rotation, integration over one hemisphere is sufficient. Therefore, $\phi_1$ ranges from 0 to $\pi/2$ only. The surface element is given by $d^3S = 8 \sin^2 \phi_1 \sin \phi_2 d\phi_1 d\phi_2 d\phi_3$, where the factor
8 = 2³ provides the necessary isotropic scaling by the factor of 2 per dimension. As such, the total volume of $SO(3)$ reads

\[
V = \int_{\phi_1=0}^{\pi/2} \int_{\phi_2=0}^{\pi} \int_{\phi_3=0}^{2\pi} 8 \sin^2 \phi_1 \sin \phi_2 d\phi_1 d\phi_2 d\phi_3 \\
= 32\pi \int_{\phi_1=0}^{\pi/2} \sin^2 \phi_1 d\phi_1 \\
= 8\pi^2,
\]

which is also intuitively accessible, as the rotation of a principal axis provides $4\pi$, i.e., the area of a 2-sphere, and a rotation around the principal axis contributes another factor of $2\pi$. Using this result, the entropy of a free rotor in three dimensions is $\log(8\pi^2)$.

To obtain the entropy of $p_1^{(\mu)}(q) = \frac{1}{Z^{(\mu)}} \cos^\mu \phi_1 = \frac{1}{Z^{(\mu)}} q_1^\mu$, it is first necessary to calculate the normalization $Z^{(\mu)}$

\[
Z^{(\mu)} = \int_{\phi_1=0}^{\pi/2} \int_{\phi_2=0}^{\pi} \int_{\phi_3=0}^{2\pi} 8 \cos^\mu \phi_1 \sin^2 \phi_1 \sin \phi_2 d\phi_1 d\phi_2 d\phi_3 \\
= 32\pi \int_{\phi_1=0}^{\pi/2} \cos^\mu \phi_1 \sin^2 \phi_1 d\phi_1 \\
= 32\pi \left[ \int_{\phi_1=0}^{\pi/2} \cos^\mu d\phi_1 - \int_{\phi_1=0}^{\pi/2} \cos^{\mu+2} \phi_1 d\phi_1 \right] \\
= 32\pi \left[ \frac{\sqrt{\pi} \Gamma \left( \frac{\mu+1}{2} \right)}{2\Gamma \left( \frac{\mu+2}{2} \right)} - \frac{\sqrt{\pi} \Gamma \left( \frac{\mu+3}{2} \right)}{2\Gamma \left( \frac{\mu+4}{2} \right)} \right] \\
= 8\pi^2 \frac{\Gamma \left( \frac{\mu+1}{2} \right)}{\Gamma \left( \frac{\mu+4}{2} \right)},
\]
where $\Gamma$ is the gamma function. The entropy of $p_1^{(\mu)}(q)$ is

$$S_1^{(\mu)} = - \langle \log p_1^{(\mu)}(q) \rangle$$

$$= \log Z^{(\mu)} - \frac{8}{Z^{(\mu)}} \int_{\phi_1=0}^{\pi/2} \int_{\phi_2=0}^{\pi} \int_{\phi_3=0}^{2\pi} \log(\cos^\mu \phi_1) \cos^\mu \phi_1 \sin^2 \phi_1 \sin \phi_2 \sin \phi_1 \sin \phi_2 \sin \phi_3$$

$$= \log Z^{(\mu)} - \frac{32\pi \mu}{Z^{(\mu)}} \int_{\phi_1=0}^{\pi/2} \log(\cos \phi_1) \cos^\mu \phi_1 \sin^2 \phi_1 d\phi_1$$

$$= \log Z^{(\mu)} - \frac{32\pi \mu}{Z^{(\mu)}} \int_{\phi_1=0}^{\pi/2} \cos^\mu \phi_1 \sin^2 \phi_1 d\phi_1$$

$$= \log Z^{(\mu)} - \frac{\mu}{Z^{(\mu)}} \frac{d}{d\mu} Z^{(\mu)}$$

$$= \log Z^{(\mu)} - \frac{\Gamma \left( \frac{\mu+1}{2} \right)}{\Gamma \left( \frac{\mu+2}{2} \right)} \frac{d}{d\mu} \Gamma \left( \frac{\mu+1}{2} \right)$$

$$= \log Z^{(\mu)} + \frac{\mu}{2} \left\{ \psi \left( \frac{\mu+4}{2} \right) - \psi \left( \frac{\mu+1}{2} \right) \right\}$$

$$= \log \left( 8\pi^2 \right) + \log \left( \frac{\Gamma \left( \frac{\mu+1}{2} \right)}{\Gamma \left( \frac{\mu+2}{2} \right)} \right) + \frac{\mu}{2} \left\{ \psi \left( \frac{\mu+4}{2} \right) - \psi \left( \frac{\mu+1}{2} \right) \right\}$$

$$= \frac{1}{2} \left\{ \mu \psi \left( \frac{\mu+4}{2} \right) - \mu \psi \left( \frac{\mu+1}{2} \right) + 2 \log \left( \frac{\Gamma \left( \frac{\mu+1}{2} \right)}{\Gamma \left( \frac{\mu+2}{2} \right)} \right) + \log \left( 64\pi^3 \right) \right\},$$

with $\Gamma$ as the gamma function and $\psi$ as the digamma function.

The normalization of $p_{2, corr}^{(\mu)}(q_1, q_2) \propto \cos^\mu (|q_1 \cdot q_2|)$ is obtained by using the translation-invariance of $q_1 \cdot q_2$ as $8\pi^2 Z^{(\mu)}$. In the same fashion, the entropy reads $S_{1, corr}^{(\mu)} = S_1^{(\mu)} + \log(8\pi^2)$.

**References**