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:

$$
\begin{aligned}
q_1 &= \cos\phi_1, \\
q_2 &= \sin\phi_1 \cos\phi_2, \\
q_3 &= \sin\phi_1 \sin\phi_2 \cos\phi_3, \\
q_4 &= \sin\phi_1 \sin\phi_2 \sin\phi_3,
\end{aligned}
$$

with $\phi_1 \in [0, \pi/2)$, $\phi_2 \in [0, \pi)$, $\phi_2 \in [0, 2\pi)$. Because, for quaternions, $\boldsymbol{q}$ and $-\boldsymbol{q}$ denote the same rotation, integration over one hemisphere is sufficient. Therefore, ϕ_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

$8 = 2^3$ provides the necessary isotropic scaling by the factor of 2 per dimension.[1] As such, the total volume of $SO(3)$ reads

$$
\begin{aligned}
V &= \int_{\phi_1=0}^{\pi/2} \int_{\phi_2=0}^{\pi} \int_{\phi_3=0}^{2\pi} 8 \sin^2 \phi_1 \sin \phi_2 d\phi_1 d\phi_2 d\phi_3 \\
&= 32\pi \int_{\phi_1=0}^{\pi/2} \sin^2 \phi_1 d\phi_1 \\
&= 8\pi^2,
\end{aligned}
$$

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

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

$$
\begin{aligned}
Z^{(\mu)} &= \int_{\phi_1=0}^{\pi/2} \int_{\phi_2=0}^{\pi} \int_{\phi_3=0}^{2\pi} 8 \cos^\mu \phi_1 \sin^2 \phi_1 \sin \phi_2 d\phi_1 d\phi_2 d\phi_3 \\
&= 32\pi \int_{\phi_1=0}^{\pi/2} \cos^\mu \phi_1 \sin^2 \phi_1 d\phi_1 \\
&= 32\pi \left[\int_{\phi_1=0}^{\pi/2} \cos^\mu d\phi_1 - \int_{\phi_1=0}^{\pi/2} \cos^{\mu+2} \phi_1 d\phi_1 \right] \\
&= 32\pi \left[\frac{\sqrt{\pi}\Gamma\left(\frac{\mu+1}{2}\right)}{2\Gamma\left(\frac{\mu+2}{2}\right)} - \frac{\sqrt{\pi}\Gamma\left(\frac{\mu+3}{2}\right)}{2\Gamma\left(\frac{\mu+4}{2}\right)} \right] \\
&= 8\pi^{\frac{3}{2}} \frac{\Gamma\left(\frac{\mu+1}{2}\right)}{\Gamma\left(\frac{\mu+4}{2}\right)},
\end{aligned}
$$

where Γ is the gamma function. The entropy of $p_1^{(\mu)}(\boldsymbol{q})$ is

$$\begin{aligned}
S_1^{(\mu)} &= -\langle \log p_1^{(\mu)}(\boldsymbol{q}) \rangle \\
&= \log Z^{(\mu)} - \frac{8}{Z^{(\mu)}} \int_{\phi_1=0}^{\pi/2} \int_{\phi_2=0}^{\pi} \int_{\phi_3=0}^{2\pi} \log(\cos^\mu \phi_1) \cos^\mu \phi_1 \sin^2 \phi_1 \sin \phi_2 d\phi_1 d\phi_2 d\phi_3 \\
&= \log Z^{(\mu)} - \frac{32\pi\mu}{Z^{(\mu)}} \int_{\phi_1=0}^{\pi/2} \log(\cos \phi_1) \cos^\mu \phi_1 \sin^2 \phi_1 d\phi_1 \\
&= \log Z^{(\mu)} - \frac{32\pi\mu}{Z^{(\mu)}} \int_{\phi_1=0}^{\pi/2} \frac{d}{d\mu} \cos^\mu \phi_1 \sin^2 \phi_1 d\phi_1 \\
&= \log Z^{(\mu)} - \frac{32\pi\mu}{Z^{(\mu)}} \frac{d}{d\mu} \int_{\phi_1=0}^{\pi/2} \cos^\mu \phi_1 \sin^2 \phi_1 d\phi_1 \\
&= \log Z^{(\mu)} - \frac{\mu}{Z^{(\mu)}} \frac{d}{d\mu} Z^{(\mu)} \\
&= \log Z^{(\mu)} - \mu \frac{\Gamma\left(\frac{\mu+4}{2}\right)}{\Gamma\left(\frac{\mu+1}{2}\right)} \frac{d}{d\mu} \frac{\Gamma\left(\frac{\mu+1}{2}\right)}{\Gamma\left(\frac{\mu+4}{2}\right)} \\
&= \log Z^{(\mu)} + \frac{\mu}{2} \left\{ \frac{\Gamma'\left(\frac{\mu+4}{2}\right)}{\Gamma\left(\frac{\mu+4}{2}\right)} - \frac{\Gamma'\left(\frac{\mu+1}{2}\right)}{\Gamma\left(\frac{\mu+1}{2}\right)} \right\} \\
&= \log Z^{(\mu)} + \frac{\mu}{2} \left\{ \psi\left(\frac{\mu+4}{2}\right) - \psi\left(\frac{\mu+1}{2}\right) \right\} \\
&= \log\left(8\pi^{\frac{3}{2}}\right) + \log\left(\frac{\Gamma\left(\frac{\mu+1}{2}\right)}{\Gamma\left(\frac{\mu+4}{2}\right)}\right) + \frac{\mu}{2} \left\{ \psi\left(\frac{\mu+4}{2}\right) - \psi\left(\frac{\mu+1}{2}\right) \right\} \\
&= \frac{1}{2} \left\{ \mu\psi\left(\frac{\mu+4}{2}\right) - \mu\psi\left(\frac{\mu+1}{2}\right) + 2\log\left(\frac{\Gamma\left(\frac{\mu+1}{2}\right)}{\Gamma\left(\frac{\mu+4}{2}\right)}\right) + \log\left(64\pi^3\right) \right\},
\end{aligned}$$

with Γ as the gamma function and ψ as the digamma function.

The normalization of $p_{2,corr}^{(\mu)}((\boldsymbol{q}_1, \boldsymbol{q}_2)) \propto \cos^\mu(|\boldsymbol{q}_1 \cdot \boldsymbol{q}_2|)$ is obtained by using the translation-invariance of $\boldsymbol{q}_1 \cdot \boldsymbol{q}_2$ 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

(1) Huynh, D. Q. Metrics for 3D rotations: Comparison and analysis. *Journal of Mathematical Imaging and Vision* **2009**, *35*, 155–164.