Rotational friction and diffusion of quantum rigid rotors — Supplemental Material

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I. EHRENFEST EQUATIONS OF MOTION

Denoting by $\mathbf{n}_i(\Omega)$ the i-th principal axis of the rotor so that $\mathbf{n}_k(\Omega)\cdot \mathrm{I}(\Omega)\mathbf{n}_j(\Omega) = I_k\delta_{kj}$, the components of the angular momentum operator in the body fixed frame are given by $\widetilde{\mathsf{J}}_k = \mathbf{n}_k \cdot \mathbf{J} = \mathbf{J}\cdot\mathbf{n}_k$ and in the space fixed frame by $\mathsf{J}_k = \mathbf{e}_k\cdot\mathbf{J}$. They obey the commutation relation $[\mathsf{J}_j,\mathsf{J}_k] = i\varepsilon_{jk\ell}\mathsf{J}_\ell$, $[\widetilde{\mathsf{J}}_j,\widetilde{\mathsf{J}}_k] = -i\varepsilon_{jk\ell}\widetilde{\mathsf{J}}_\ell$ and $[\mathsf{J}_j,\widetilde{\mathsf{J}}_k]=0$. Their commutation relations with the rotation matrix $\mathrm{R}(\Omega)$ can be expressed as

$$[\mathsf{J}_k,\mathrm{R}(\Omega)] = \frac{\hbar}{i}\mathbf{e}_k\times\mathrm{R}(\Omega) \tag{S1}$$

$$[\widetilde{\mathsf{J}}_k,\mathrm{R}(\Omega)] = \frac{\hbar}{i}\mathbf{n}_k(\Omega)\times\mathrm{R}(\Omega). \tag{S2}$$

Using these commutators repeatedly one obtains (2) from the master equations (8) and (10).

For illustration, the dynamics of the first moment of the angular momentum operator due to (11) is

$$\partial_t\langle\mathsf{J}_k\rangle = \frac{2D}{\hbar^2}\left\langle\mathbf{m}(\Omega)\cdot\mathsf{J}_k\mathbf{m}(\Omega)-\mathsf{J}_k\right\rangle - \frac{i\Gamma}{2\hbar}\left\langle\mathbf{m}(\Omega)\cdot\mathsf{J}_k\mathbf{m}(\Omega)\times\mathbf{J}+\mathbf{J}\times\mathbf{m}(\Omega)\cdot\mathsf{J}_k\mathbf{m}(\Omega)\right\rangle + \mathcal{O}\left(\frac{\hbar^2}{k_\mathrm{B}TI}\right). \tag{S3}$$

Using Eq. (S1) with $\mathbf{m}(\Omega) = \mathrm{R}(\Omega)\mathbf{e}_z$, the first term vanishes and the second evaluates to $-\Gamma\langle\mathsf{J}_k\rangle$, in accordance with (2). The calculation of the second moments follows the same lines.

II. LINEAR AND PLANAR ROTOR THERMAL STATE

In order to determine the stationary state of the linear rotor we consider (10) in the angular momentum eigenbasis $|\ell m\rangle$ and evaluate the matrix elements $M^{\ell''m''}_{\ell m\ell'm'}$ defined via

$$\langle\ell m\,|\,\mathcal{D}\rho_\mathrm{eq}\,|\,\ell'm'\rangle = \sum_{\ell''=0}^{\infty}\sum_{m''=-\ell''}^{\ell''}\rho_\mathrm{eq}^{\ell''m''}M^{\ell''m''}_{\ell m\ell'm'}. \tag{S4}$$

Here we used that ρ_eq is diagonal in the angular momentum basis. The matrix elements $M^{\ell''m''}_{\ell m\ell'm'}$ can be computed by using the properties of spherical harmonics,

$$\mathsf{J}_1\,|\ell m\rangle = \frac{\hbar}{2}\left(c_+\,|\ell m+1\rangle + c_-\,|\ell m-1\rangle\right), \tag{S5a}$$

$$\mathsf{J}_2\,|\ell m\rangle = \frac{\hbar}{2i}\left(c_+\,|\ell m+1\rangle - c_-\,|\ell m-1\rangle\right), \tag{S5b}$$

$$\mathsf{J}_3\,|\ell m\rangle = \hbar m\,|\ell m\rangle, \tag{S5c}$$

with $c_\pm = \sqrt{\ell(\ell+1)-m(m\pm1)}$, as well as the representation of matrix elements in terms of Wigner 3-j symbols,

$$\langle\ell m\,|\,Y_{\ell'',m''}(\beta,\alpha)\,|\,\ell'm'\rangle = \sqrt{\frac{(2\ell+1)(2\ell'+1)(2\ell''+1)}{4\pi}}\begin{pmatrix}\ell & \ell' & \ell''\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell & \ell' & \ell''\\ -m & m' & m''\end{pmatrix}. \tag{S6}$$

The latter vanishes unless $m-m'-m''=0$ and $\ell+\ell'+\ell''$ is even, providing selection rules for the computation of the matrix elements. These selection rules imply that the off-diagonal elements of $\langle\ell m\,|\,\mathcal{D}\rho_\mathrm{eq}\,|\,\ell'm'\rangle$ vanish so that one has for all ℓ, m

$$\sum_{\ell''=0}^{\infty}\sum_{m''=-\ell''}^{\ell''}\rho_\mathrm{eq}^{\ell''m''}M^{\ell''m''}_{\ell m\ell m} = 0. \tag{S7}$$

Only a finite number of terms $\rho_{\rm eq}^{\ell''m''}$ are coupled due to the selection rules. Starting with the equation for $\ell = 0$ and $m = 0$ one can construct the solution iteratively, arriving at Eq. (13).

The same procedure can be used to calculate the stationary solution of the planar rotor. However, in this case one needs only the matrix elements

$$\langle m \,|\, \cos \alpha \,|\, m' \rangle = \frac{1}{2} \left(\delta_{mm+1} + \delta_{mm-1} \right), \tag{S8}$$

along with $\mathsf{p}_\alpha \,|m\rangle = \hbar m \,|m\rangle$. Again, this yields a set of equations that can be solved by iteration starting from $m = 0$.

III. THERMALIZATION OF ASYMMETRIC ROTORS

We show that the Gibbs state of the asymmetric rotor is a stationary solution of (8) for large temperatures. Note that the limit of large temperatures, $\hbar^2/k_{\rm B}TI_{\rm min} \to 0$ with $I_{\rm min}$ the smallest moment of inertia, is equivalent to the semiclassical limit.

We first define the transformation

$$F(\mathbf{A}_k) = e^{-\mathsf{H}/k_{\rm B}T} \mathbf{A}_k e^{\mathsf{H}/k_{\rm B}T} = \sum_{n=0}^{\infty} \frac{(-k_{\rm B}T)^{-n}}{n!} \left[\mathsf{H}, \mathbf{A}_k\right]_n, \tag{S9}$$

where $[\mathsf{A},\mathsf{B}]_n = [\mathsf{A},[\mathsf{A},\ldots,[\mathsf{A},\mathsf{B}]\ldots]]$ denotes the n-fold commutator. Note that $F(\mathbf{A}_k \cdot \mathbf{A}_\ell) = F(\mathbf{A}_k) \cdot F(\mathbf{A}_\ell)$ and $F(\mathbf{A}_k^\dagger) \neq F(\mathbf{A}_k)^\dagger$. With this mapping each summand of the dissipator (8) acting on the Gibbs state can be rewritten as

$$\begin{aligned} \mathcal{D}_k \frac{e^{-\mathsf{H}/k_{\rm B}T}}{Z} =& \frac{2\widetilde{D}_k}{\hbar^2} \left(\mathbf{A}_k \cdot \frac{e^{-\mathsf{H}/k_{\rm B}T}}{Z} \mathbf{A}_k^\dagger - \frac{1}{2} \mathbf{A}_k^\dagger \cdot \mathbf{A}_k \frac{e^{-\mathsf{H}/k_{\rm B}T}}{Z} - \frac{1}{2} \frac{e^{-\mathsf{H}/k_{\rm B}T}}{Z} \mathbf{A}_k^\dagger \cdot \mathbf{A}_k \right) \\ =& \frac{2\widetilde{D}_k}{\hbar^2} \left[\mathbf{A}_k \cdot F(\mathbf{A}_k^\dagger) - \frac{1}{2} \mathbf{A}_k^\dagger \cdot \mathbf{A}_k - \frac{1}{2} F(\mathbf{A}_k^\dagger \cdot \mathbf{A}_k) \right] \frac{e^{-\mathsf{H}/k_{\rm B}T}}{Z}. \end{aligned} \tag{S10}$$

Inserting the expansion (S9) into (S10) and sorting the terms in the square brackets in orders of $1/T$ shows that the zeroth and first order term vanish and, taking the temperature-dependence of the prefactor into account, the remainder decreases at least as $1/T$.

IV. FOKKER-PLANCK EQUATION OF RIGIDLY CONNECTED CLASSICAL PARTICLES

We consider N point particles of mass m_n, position $\mathbf{r}_n$ and momentum $\mathbf{p}_n$, in an environment of temperature T. Denoting the friction and diffusion constant of the n-th particle by γ_n and $D_n = k_{\rm B}Tm_n\gamma_n$, respectively, the Fokker-Planck equation for the total phase space distribution function $f_t(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)$ reads as

$$\partial_t^{\rm nc} f_t = \sum_{n=1}^{N} \gamma_n \left[\nabla_{\mathbf{p}_n} \cdot (\mathbf{p}_n f_t) + k_{\rm B}Tm_n \nabla_{\mathbf{p}_n}^2 f_t \right]. \tag{S11}$$

This assumes that the diffusion process is isotropic.

We now invoke that the particles are rigidly connected and that their center-of-mass is fixed at the origin, so that the positions $\mathbf{r}_n$ are determined by the rotation matrix, $\mathbf{r}_n = \mathrm{R}(\Omega)\mathbf{r}_n^{(0)}$. One thus obtains for the momenta $\mathbf{p}_n = m_n \mathrm{I}^{-1}(\Omega)\mathbf{J} \times \mathbf{r}_n$ with $\mathbf{J} = \sum_n \mathbf{r}_n \times \mathbf{p}_n$. Exploiting that

$$\nabla_{\mathbf{p}_n} = (\nabla_{\mathbf{p}_n} \otimes \mathbf{J}) \nabla_{\mathbf{J}} = -\mathbf{r}_n \times \nabla_{\mathbf{J}} \tag{S12}$$

yields from (S11) the rotational Fokker-Planck equation (1) with the rigid rotor distribution $h_t(\Omega, \mathbf{J})$. The corresponding rotational diffusion tensor can thus be identified as

$$\mathrm{D}(\Omega) = k_{\rm B}T \sum_{n=1}^{N} m_n \gamma_n \left(r_n^2 \mathbb{1} - \mathbf{r}_n \otimes \mathbf{r}_n \right). \tag{S13}$$

It is related to the friction tensor by $\mathrm{D}(\Omega) = k_{\mathrm{B}}T\Gamma(\Omega)\mathrm{I}(\Omega)$.

Note that the eigenvalues of the rotational diffusion tensor (S13) fulfill the inequality $D_i + D_j \geq D_k$ for (i,j,k) permutations of $(1,2,3)$, as can be seen from tracing over (S13) and deducing that

$$\sum_{n=1}^{N} m_n \gamma_n \mathbf{r}_n \otimes \mathbf{r}_n = \frac{1}{2}\mathrm{tr}[\mathrm{D}(\Omega)]\mathbb{1} - \mathrm{D}(\Omega) > 0. \tag{S14}$$

This constraint for the possible values of the diffusion coefficients can be relaxed by allowing for directed diffusion in Eq. (S11). Specifically, replacing the second derivatives $\nabla^2_{\mathbf{p}_n}$ in the last term by $(\mathbf{n}_n \cdot \nabla_{\mathbf{p}_n})^2$, so that the (particle- and orientation-dependent) unit vectors $\mathbf{n}_n$ define the direction of diffusion, results in the same Fokker-Planck equation (1) but with the diffusion tensor

$$\mathrm{D}(\Omega) = k_{\mathrm{B}}T \sum_{n=1}^{N} \gamma_n m_n \left(\mathbf{n}_n \times \mathbf{r}_n\right) \otimes \left(\mathbf{n}_n \times \mathbf{r}_n\right) \tag{S15}$$

and the corresponding friction tensor. Its eigenvalues can take arbitrary, positive values, depending on the m_n, γ_n, $\mathbf{n}_n$ and $\mathbf{r}_n$.

V. INVERSION SYMMETRIC PARTICLES

The master equation (10) presupposes that the particle-bath interaction is isotropic. An inversion-symmetric particle prepared in a coherent superposition of the opposite orientations $\mathbf{m}(\Omega)$ and $-\mathbf{m}(\Omega)$ is predicted to decohere because the localization rate (12) is not zero, even if these orientations are indistinguishable by the environment. Since this symmetry enters only on the quantum level it must not affect the semiclassical limit.

The dissipator for inversion-symmetric particles can be obtained by generalizing the microscopic derivation of inversion symmetric angular momentum diffusion [Papendell *et al.*, New J. Phys. **19**, 122001 (2017)]. The Lindblad operators must then be quadratic in the particle orientation in order to preserve inversion symmetry. This yields

$$\mathcal{D}\rho = \frac{D}{\hbar^2}\mathrm{Tr}\left[\mathsf{B}\rho\mathsf{B}^\dagger - \frac{1}{2}\left\{\mathsf{B}^\dagger\mathsf{B}, \rho\right\}\right], \tag{S16a}$$

where $\mathrm{Tr}(\cdot)$ denotes the matrix trace (not to be confused with the operator trace) and the tensor Lindblad operators are

$$\mathsf{B} = \mathbf{m}(\Omega) \otimes \mathbf{m}(\Omega) - \frac{i\hbar}{2k_{\mathrm{B}}T}\mathbf{m}(\Omega) \otimes \mathbf{m}(\Omega) \times \mathrm{I}^{-1}(\Omega)\mathbf{J}. \tag{S16b}$$

While the first term appears already in the article by Papendell *et al.*, the second results from quantizing the time derivative $\partial_t[\mathbf{m}(\Omega) \otimes \mathbf{m}(\Omega)]$. The latter can be expressed as $\mathbf{m}(\Omega) \otimes \mathbf{m}(\Omega) \times \mathrm{I}^{-1}(\Omega)\mathbf{J}$ because of the matrix trace in (S16a) without affecting diffusion and friction.

The dissipator (S16) preserves inversion symmetry and implies the moment equations of motion (2) as well as the thermalization (3) and (4). In addition, it also leads to the Fokker-Planck equation (1). The T-independent contribution of (S16b) depends only on the orientation operator and thus leads to orientational decoherence and angular momentum diffusion. The corresponding decoherence rate

$$F(\Omega, \Omega') = \frac{k_{\mathrm{B}}T\mathit{\Gamma} I}{\hbar^2}|\mathbf{m}(\Omega) \times \mathbf{m}(\Omega')|^2, \tag{S17}$$

vanishes not only for $\Omega = \Omega'$ but also for a superpositions between opposite orientations. The quantum phase space dynamics of the inversion-symmetric planar rotor can be obtained from Eq. (10) by replacing $\mathit{\Gamma}$ by $\mathit{\Gamma}/2$, D by $D/4$ and $m \pm 1$ by $m \pm 2$.