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Equations of Motion for Rotational Motion in Liquids

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The equations of motion corresponding to master equations describing rotational relaxation in liquids are shown to be purely deterministic and, in general, nonlocal in time.

KEY WORDS: Stochastic; master equation; rotational relaxation; liquids.

Stochastic equations are often used in the description of molecular motion in liquids. Two equivalent approaches are via the equation of motion for the variable of interest, and via an equation for the probability distribution function of this variable, i.e., a master equation.(1) For example, the translational motion of a particle in the fluid can be described by the Debye diffusion equation.(2) The motion can also be described by a linear Langevin equation with delta-correlated Gaussian noise.(1,3)

Rotational motion in liquids is often described by master equations for the probability distribution of molecular orientation.(4) Debye, in analogy to the translational description, presented a rotational diffusion equation for this probability.(2) Since his work, a variety of generalizations have appeared in the literature.(4) It is the purpose of this note to find the equations of motion for the orientational variables.

All models of rotational relaxation in fluids must reflect the rotational isotropy of the fluid. This implies that the reorientational transition probabilities appearing in any master equation must only be functions of orientation changes and not of absolute orientations. We have shown that the Wigner

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rotation matrices⁽⁵⁾ are therefore eigenfunctions of the transition probabilities.⁽⁶⁾ Calculation of correlation functions of experimental interest which involve Wigner rotation matrices is greatly simplified by this result.

Rotational isotropy then also implies a particularly simple form for the equations of motion describing the time development of the rotation matrices. Since the rotation matrices are normal modes of the system, we will show that their equations of motion are deterministic, the absence of a "random force" term arising from the lack of coupling between the modes. The equations of motion are, however, nonlocal in time.

For simplicity we shall demonstrate these features for a fluid with one orientation variable described by the master equation⁽⁴⁾

$$\partial P(\theta, t|\theta_0)/\partial t = \int_0^{2\pi} d\theta' \int_0^t d\tau\, A(\theta - \theta'; t - \tau)P(\theta', \tau|\theta_0) \tag{1}$$

Here $P(\theta, t|\theta_0)$ is the conditional probability that the orientation is θ at time t given that it is initially θ_0, and $A(\theta - \theta'; t - \tau)$ is the transition rate from θ' to θ in time $t - \tau$. The analysis below can also be carried out for a fluid with Euler angles as orientation variables and a more complex dynamical behavior than that implicit in Eq. (1).⁽⁴⁾

Equation (1) can be rewritten as a Kramers–Moyal expansion⁽⁷⁾

$$\partial P(\theta, t|\theta_0)/\partial t = \sum_{n=1}^{\infty} \int_0^t d\tau\, \alpha_n(t - \tau)(\partial^n/\partial\theta^n)P(\theta, \tau|\theta_0) \tag{2}$$

where

$$\alpha_n(t) = (1/n!) \int_0^{2\pi} d\theta'\, (\theta - \theta')^n A(\theta - \theta'; t) \tag{3}$$

We define an operator $\mathbf{A}(t)$ by the equation

$$\partial P(\theta, t|\theta_0)/\partial t = \int_0^t d\tau\, \mathbf{A}(t - \tau)P(\theta, \tau|\theta_0) \tag{4}$$

Comparison of the Laplace transforms of Eqs. (2) and (4) leads to

$$\hat{P}(\theta, s|\theta_0) = [s - \hat{\mathbf{A}}(s)]^{-1}\, \delta(\theta - \theta_0) \tag{5}$$

with

$$\hat{\mathbf{A}}(s) = \sum_{n=1}^{\infty} \hat{\alpha}_{2n}(s)(\partial^{2n}/\partial\theta^{2n}) \tag{6}$$

Here we have noted that $\alpha_n(t) = 0$ for all odd n.

In a one-variable description the Wigner rotation matrices reduce to $(2\pi)^{-1/2}\exp(ik\theta)$, where k is an integer.⁽⁵⁾ Thus the correlation functions of physical interest are

$$C_k(t) = (1/2\pi)\langle e^{ik\theta(t)}e^{-ik\theta_0}\rangle$$
$$= (1/2\pi)\int_0^{2\pi} d\theta \int_0^{2\pi} d\theta_0\, e^{ik\theta}e^{-ik\theta_0}P(\theta, t\,|\,\theta_0) \qquad (7)$$

Use of Eqs. (5) and (6) in the Laplace transform of Eq. (7) and repeated integrations by parts yields

$$\hat{C}_k(s) = (1/2\pi)\int_0^t d\theta\, e^{-ik\theta}[s - \hat{\mathbf{A}}(s)]^{-1}e^{ik\theta} \qquad (8)$$

It is convenient to work with the state $|k\rangle$ of which $(2\pi)^{-1/2}\exp(ik\theta)$ is the orientation representation. In terms of creation and annihilation operators $a^\dagger|k\rangle = |k + 1\rangle$ and $a|k\rangle = k|k - 1\rangle$, Eqs. (6) and (8) can be written as

$$\hat{\mathbf{A}}(s) = \sum_{n=1}^{\infty} (-1)^n \hat{\alpha}_{2n}(s)(a^\dagger a)^{2n} \qquad (9)$$

and

$$\hat{C}_k(s) = \langle k|ks\rangle \qquad (10)$$

where

$$|ks\rangle = [s - \hat{\mathbf{A}}(s)]^{-1}|k\rangle \qquad (11)$$

In order to obtain an equation of motion for the time evolution of the state $|k\rangle$, we note that the Laplace transform of the time derivative $(d/dt)|kt\rangle$ is

$$s|ks\rangle - |k\rangle = [s - \hat{\mathbf{A}}(s)]^{-1}\hat{\mathbf{A}}(s)|k\rangle \qquad (12)$$

We define a projection operator

$$\mathbf{P}_k \equiv |k\rangle\langle k| \qquad (13)$$

which projects the initial contribution of state $|k\rangle$ from an arbitrary state.⁽⁸⁾ The use of the identity

$$[s - (1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)]^{-1}$$
$$= [s - \hat{\mathbf{A}}(s)]^{-1} - [s - \hat{\mathbf{A}}(s)]^{-1}\mathbf{P}_k\hat{\mathbf{A}}(s)[s - (1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)]^{-1} \qquad (14)$$

on the decomposition $\hat{\mathbf{A}}(s)|k\rangle = \mathbf{P}_k\hat{\mathbf{A}}(s)|k\rangle + (1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)|k\rangle$ leads to the equation of motion

$$s|ks\rangle - |k\rangle = \hat{\Omega}_{kk}(s)|ks\rangle + \hat{\Delta}_{kk}(s)|ks\rangle + |\hat{F}_k(s)\rangle \qquad (15)$$

where

$$\hat{\Omega}_{kk}(s) = \langle k|\hat{\mathbf{A}}(s)|k\rangle \tag{16}$$

$$\hat{\Delta}_{kk}(s) = \langle k|\hat{\mathbf{A}}(s)(1 - \mathbf{P}_k)[s - (1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)]^{-1}(1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)|k\rangle \tag{17}$$

and

$$|\hat{F}_k(s)\rangle = [s - (1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)]^{-1}(1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)|k\rangle \tag{18}$$

From Eq. (9) it follows that $|k\rangle$ is an eigenstate of $\hat{\mathbf{A}}(s)$ and hence $(1 - \mathbf{P}_k)\hat{\mathbf{A}}(s)|k\rangle = 0$. Therefore the equation of motion reduces to

$$s|ks\rangle - |k\rangle = \hat{\Omega}_{kk}(s)|ks\rangle \tag{19}$$

or, inverse-transforming,

$$(d/dt)e^{ik\theta(t)} = \int_0^t d\tau\, \Omega_{kk}(t - \tau)e^{ik\theta(\tau)} \tag{20}$$

The equation of motion for the variable $\exp(ik\theta)$ is completely deterministic with a memory kernel defined in terms of the transition rate $A(\theta, t)$. This result is not unexpected since the master equation, Eq. (1), implies that we have averaged over the bath variables (the phase space coordinates of all the particles except for the "test" particle) *and also* over the position, momentum, and angular momentum of the test particle. Thus, the only opportunity for a random force term is via mode coupling contained in the $\hat{\Delta}_{kk}(s)$ and $|F_k(s)\rangle$ terms. The rotational invariance of $A(\theta, t)$ ensures that the modes $e^{ik\theta}$ obey uncoupled equations for each k and hence there is no mode coupling here. The kernel in Eq. (20) is nonlocal in time because we used a non-Markovian transition rate, not because of mode coupling.

It may readily be verified that the correlation function also obeys Eq. (20). The time course of the correlation function is determined by $\Omega_{kk}(t)$, a result completely equivalent to the master equation description.(4)

It should be noted that the equation of motion for the variable θ would not be closed. Rather, it would exhibit an additional term due to mode coupling.

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