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# Coupled translational and rotational diffusion in liquids

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The equations for coupled translational and rotational diffusion of asymmetric molecules immersed in a fluid are obtained. The method used begins with the Kramers–Liouville equation and leads to the generalized Smoluchowski equation for diffusion in the presence of potentials. Both external potentials and intermolecular potentials are considered. The contraction of the description from the Kramers–Liouville equation to the Smoluchowski equation is achieved by using a combination of operator calculus and cumulants. Explicit solutions to these equations are obtained for the two-dimensional case. Comparison of our results with earlier literature is also presented.

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## I. INTRODUCTION

In this paper we study the translational and rotational motion of molecules immersed in a fluid. The molecules experience translational and rotational Brownian motion as a result of the bombardment by fluid molecules. The description of this essentially stochastic process in terms of the probability-distribution function $P(t,x)$ leads to a diffusion equation

$$\frac{\partial}{\partial t} P(t,x) = \sum_{i,j} a_{ij}(x) \frac{\partial^2}{\partial x_i \partial x_j} P(t,x) + \sum_i b_i(x) \frac{\partial}{\partial x_i} P(t,x) \equiv A P(t,x) \tag{1}$$

for all times $t \geqslant 0$ and all points $x$, $x = (q_1, q_2, q_3, \phi, \theta, \psi)$. $q = (q_1, q_2, q_3)$ describe the position and the Euler angles $\alpha = (\phi, \theta, \psi)$ fix the orientation. The differential operator $A$ is a diffusion operator. All eigenvalues of the symmetric matrix $[a_{ij}(x)]$ are non-negative. For translational diffusion $A_T$ is simply a diffusion constant multiplied by the Laplace operator. Favro[1] derived the diffusion equation for rotational Brownian motion and was able to solve it for axial symmetric molecules using the fact that the diffusion operator $A_R$ has the same form as the quantum mechanical Hamilton operator for a rigid body,[2] the properties of which are well known. In general the translational and rotational motions are coupled in a complicated way.

Already 50 years ago, Kolmogorov showed that under very general conditions a Markov process defined in terms of the transition probability $F(t,x,x')dx'$ of finding a particle initially at point $x$ in the infinitesimal small set $dx'$ after a lapse of time $t$, leads to a diffusion equation. The probability density

$$P(t,x) \equiv \int_{S_x} F(t,x',x) P(0,x')\, dx' \tag{2}$$

satisfies Eq. (1). $S_x$ is the space containing all points $x$. $P(0,x)$ is the initial distribution at time $t = 0$.

The concept of a Markov process is an idealization of the underlying physical reality. For a complete dynamical description, it is necessary to consider the distribution function $f_c(t,x_c,y_c)$ defined on the phase space $S_{x_c} \times S_{y_c}$ consisting of all points $(x_c, y_c)$ with $x_c = (q_1, q_2, q_3, \phi, \theta, \psi)$ and the canonically conjugate momenta $y_c = (p_1, p_2, p_3, p_\phi, p_\theta, p_\psi)$. The distribution function $f_c(t,x_c,y_c)$ satisfies the Kramers–Liouville equation[3,4]

$$\frac{\partial}{\partial t} f_c(t,x_c,y_c) = (L + K) f_c(t,x_c,y_c). \tag{3}$$

$L$ is Liouville's operator and $K$ denotes Kramers operator, which describes the effect of all random forces acting on the Brownian particle. If Eq. (3) can be solved for some initial distribution $f_c(0,x_c,y_c)$ then it is possible to find an operator $G(t,x_c)$ such that the averaged distribution $P(t,x_c)$ defined by

$$P(t,x_c) \equiv \int_{S_{y_c}} dy_c\, f_c(t,x_c,y_c) \tag{4}$$

fulfills the first order differential equation in time:

$$\frac{\partial}{\partial t} P(t,x_c) = G(t,x_c) P(t,x_c). \tag{5}$$

In general nothing is gained, since $G(t,x_c)$ might be a very complicated operator. We will use the cumulant expansion[5,6] to approximate the operator $G(t,x_c)$.

$$G(t,x_c) = \sum_{n=1}^{\infty} G^{(n)}(t,x_c). \tag{6}$$

It turns out, that the diffusion operator $A$ is the first nonvanishing term in the expansion (6). Equation (1), where $A$ is now replaced by the second cumulant $G^{(2)}(t,x_c)$ $[G^{(1)}(t,x_c) = 0]$, is a very good approximation of (5). $K$ describes the time evolution of the distribution of the momenta due to random forces. The momenta $y_c(t)$ can be considered as random variables, which very quickly become independent. $y_c(t)$ is independent of $y_c(t + \Delta t)$ if the lapse of time $\Delta t$ is large compared with the correlation time $\tau_k$. It can be shown,[7] that the $n$th cumulant is proportional to

$$G^{(n)} \sim \hat{\tau}^{n-1}. \tag{7}$$

$\hat{\tau}$ is a dimensionless quantity. $\hat{\tau} \equiv \tau_k / \tau$. $\tau$ is some typical macroscopic time unit.

Intuitively, it is clear that we obtain a Markov process on $S_x$ described by (1) if the correlation time $\tau_k$ of the momenta $y_c(t)$ becomes very small. It is the short correlation time which makes the higher order contributions small.

The idea of deriving the diffusion operator $A$ as the lowest order of a cumulant expansion (6) is not new. The actual calculation of the operators $A, G^{(3)}, \ldots$, is complicated by the nonlinearity of the equation of motion for a rigid body. The time derivatives of the angular momentum $L'$ and translational momentum $p'$ expressed in an orthogonal coordinate frame attached to the moving particle are

$$\dot{L}' = L' \times I^{-1} L' + N',$$
$$\dot{p}' = p' \times I^{-1} L' + F'. \tag{8}$$

$N'$ and $F'$ are the torques and the forces acting on the particle. The prime denotes vectors in the body fixed coordinate frame. $I$ is the tensor of inertia. It is necessary to choose body fixed coordinates for both $L'$ and $p'$ since otherwise the friction tensor $C$ depends on the orientation [see (70)].[8]

The purpose of this work is to analyze the rotational and translational diffusion in the most general case using a mathematically transparent method. We will show that

(i) The generalized Smoluchowski equation is the lowest order contribution of $G(t,x_c)$. Starting off with a Maxwell distribution at time $t=0$ the diffusion tensor is time dependent. For $t<\tau_k$ the diffusion tensor depends on the mass and the moments of inertia, and becomes stationary for $t \gg \tau_k$.

(ii) The diffusion equation couples the translational and rotational degrees of freedom even in the simplest case.[8] As an illustration, the two dimensional diffusion equation is solved. The solutions are obtained in terms of exponential and Mathieu functions. (Sec. V).

(iii) A suspension of $N$ interacting Brownian particles leads to a diffusion equation for the $N$ particle density $P(t,x_c^{(1)},x_c^{(2)},\ldots,x_c^{(N)})$. (Sec. IV).

In Sec. II the operator calculus used later is introduced and applied to the translational motion. Section III treats coupled translational and rotational diffusion.

## II. OPERATOR CALCULUS, TRANSLATIONAL DIFFUSION

The starting point of the theory is the Kramers–Liouville equation.[3,4]

$$\frac{\partial}{\partial t} f(t,q,p) = B f(t,q,p) = (L+K) f(t,q,p). \tag{9}$$

$q$ are the coordinates describing the position, $q=(q_1,q_2,q_3)$ and $p$ are the conjugate momenta. Liouville's operator is

$$Lf = -m^{-1} p \cdot \frac{\partial}{\partial q} f + \frac{\partial U}{\partial q} \cdot \frac{\partial}{\partial p} f. \tag{10}$$

$U$ denotes the potential. Kramers operator is

$$Kf = \alpha \frac{\partial}{\partial p} \cdot \left( m^{-1} p + kT \frac{\partial}{\partial p} \right) f. \tag{11}$$

It is convenient[3] to work in the "interaction picture"

$$f \equiv e^{tK} \tilde{f}. \tag{12}$$

The exponential $e^{tK}$ is defined by a formal power series in $tK$ and acts on the new function $\tilde{f}$ which is assumed to be smooth enough, such that the series $e^{tK}\tilde{f} \equiv \Sigma_{n=0}^{\infty} [(tK)^n/n!]\tilde{f}$ converges. The smoother $\tilde{f}$ the smaller the contribution of $(tK)^n$ which is a differential operator of order $2n$ in the variable $p$. The time evolution for $\tilde{f}$ is governed by the Kramers–Liouville equation in the "interaction picture".

$$\frac{\partial}{\partial t} \tilde{f} = e^{-tK} L e^{tK} \tilde{f} \equiv \tilde{L}(t) \tilde{f}. \tag{13}$$

The operator $\tilde{L}(t)$ can be expressed in terms of the differential operators $\partial/\partial q$ and $\partial/\partial p$ using the identity

$$e^{-tK} L e^{tK} = e^{-[K,\cdot]t} L. \tag{14}$$

The proof of this equation is found in Ref. 5. The operator on the right hand side is by definition

$$e^{-[K,\cdot]t} L \equiv L + \sum_{n=1}^{\infty} [K,\cdot]^n L \, [(-t)^n/n!]. \tag{15}$$

The commutators $[K,\cdot]^n L$ can be defined by recursion,

$$[K,\cdot]^1 L \equiv [K,L],$$
$$[K,\cdot]^2 L \equiv [K,[K,L]], \tag{16}$$
$$[K,\cdot]^n L \equiv [K,\cdot]([K,\cdot]^{n-1} L).$$

We can calculate all terms in the infinite sum (15). Applying the commutator algebra discussed in Ref. 3 leads to

$$\tilde{L}(t) = -e^{-(\alpha/m)t} \frac{\partial}{\partial q} \cdot \left( \frac{p}{m} + kT \frac{\partial}{\partial p} \right) + e^{(\alpha/m)t} \frac{\partial}{\partial p} \cdot \left( \frac{\partial U}{\partial q} + \frac{\partial}{\partial q} \right). \tag{17}$$

In Sec. III the corresponding expression for translational and rotational motion is derived in great detail.

Formally, the solution of (13) can be written

$$\tilde{f}(t) = E(t)\tilde{f}_0 \equiv \underset{\leftarrow}{T} \exp \int_0^t ds\, \tilde{L}(s) \tilde{f}_0, \tag{18}$$

in which $\underset{\leftarrow}{T}$ exp is the time ordered exponential.[5] $\tilde{f}_0$ is the initial distribution. The time ordered exponential must be used because $\tilde{L}(t_1)$ does not commute with $\tilde{L}(t_2)$ if $t_1 \neq t_2$. We would like to derive the time evolution for the averaged distribution $P(t,q)$,

$$P(t,q) \equiv \int d^3p\, f(t,q,p) = \int d^3p\, e^{tK} \tilde{f}(t,q,p)$$
$$= \int d^3p\, \tilde{f}(t,q,p) \equiv \langle \tilde{f}(t,q) \rangle. \tag{19}$$

The third equality can be proved by expanding the exponential $e^{tK}$. After integrating by parts, all but the lowest order term, which is $\tilde{f}$, vanish. We can assume that $\tilde{f}(t,q,p)|_{p_i=\infty} = 0$.

We write the initial condition $\tilde{f}(0,q,p) \equiv \tilde{f}_0(q,p) = f_0(q,p)$ in the form

$$f_0(q,p) = g(q,p) P_0(q),$$
$$P_0(q) = \langle f_0(q) \rangle. \tag{20}$$

With Eqs. (18)–(20) one obtains

$$P(t,q) = \int d^3p\, \tilde{f}(t,q,p)$$
$$= \int d^3p\, E(t) g(q,p) P_0(q) \tag{21}$$
$$\equiv \langle E(t) \rangle_g P_0(q).$$

The operator $\langle E(t)\rangle_g$ is obtained by multiplying $g(q,p)$ from the left with $E(t)$ and integrating over the momenta $p$. Differentiating Eq. (21) with respect to $t$ gives the time evolution equation

$$\frac{\partial}{\partial t} P(t,q) = \left(\frac{\partial}{\partial t}\langle E(t)\rangle_g\right)\langle E(t)\rangle_g^{-1} P(t,q). \tag{22}$$

We expect that the inverse $\langle E(t)\rangle_g^{-1}$ exists at least for small times. It may be obtained by the Neumann series[9] $A^{-1} = \Sigma_{n=0}^{\infty}(1-A)^n$. The operator

$$G(t,q) \equiv \left(\frac{\partial}{\partial t}\langle E(t)\rangle_g\right)\langle E(t)\rangle_g^{-1},$$
$$\frac{\partial}{\partial t} P(t,q) = G(t,q)P(t,q), \tag{23}$$

depends on $q$ since $g(q,p)$ is a function on $q$ and $p$. But in most physical applications the initial distribution of the momenta does not depend on the position $q$. In this case the operator $G$ depends only on $t$.

In order to calculate $G(t)$ we use the cumulant expansion,[5–7] which is obtained by reordering the expression

$$G(t) = \sum_{n=0}^{\infty}\left\langle \tilde{L}(t) \overset{\leftarrow}{T} \exp \int_0^t \tilde{L}(s)ds\right\rangle_g \left\langle 1 - \overset{\leftarrow}{T} \exp \int_0^t \tilde{L}(s)ds\right\rangle_g^n,$$
$$G(t) = \sum_{l=1}^{\infty} G^{(l)}. \tag{24}$$

Compare (18), (22), (23). $G^{(l)}$ contains all terms of the sum in (24) which are of order $l$ in the operator $\tilde{L}(s)$. The two lowest order terms are

$$G^{(1)}(t) = \langle \tilde{L}(t)\rangle_g = \int d^3p\, \tilde{L}(t)\, g(p),$$
$$G^{(2)}(t) = \int_0^t ds \langle \tilde{L}(t)\tilde{L}(s)\rangle_g - \int_0^t ds \langle \tilde{L}(t)\rangle_g \langle \tilde{L}(s)\rangle_g$$
$$= \int_0^t ds \int d^3p\, \tilde{L}(t)\tilde{L}(s) g(p) - \int_0^t ds \int d^3p\, \tilde{L}(t)\, g(p) \int d^3p' \tilde{L}(s)\, g(p'). \tag{25}$$

The higher order terms are given in Sec. VI.

We assume that the distribution in the momenta is initially a Maxwell distribution

$$g(p) = (2\pi mkT)^{-3/2} \exp(-p^2/2mkT). \tag{26}$$

In this case, it is easy to verify that the first cumulant $G^{(1)}(t)$ vanishes for all times $t \geqslant 0$. The second cumulant is

$$G^{(2)}(t) = \frac{kT}{\alpha}\frac{\partial}{\partial q}\cdot\left(\frac{1}{kT}\frac{\partial U}{\partial q} + \frac{\partial}{\partial q}\right)(1 - e^{-(\alpha/m)t}). \tag{27}$$

The time evolution equation (23) is, to second order in $\tilde{L}$, the Smoluchowski equation with time-dependent diffusion "constant",

$$A(t) = \frac{kT}{\alpha}(1 - e^{-(\alpha/m)t}),$$
$$\frac{\partial}{\partial t} P(t,q) = \frac{\partial}{\partial q}\cdot A(t)\left(\frac{1}{kT}\frac{\partial U}{\partial q} + \frac{\partial}{\partial q}\right) P(t,q). \tag{28}$$

At $t = 0$ the diffusion constant vanishes since by assumption the distribution in $p$ was given by a symmetric function, the Maxwell distribution. After a short time of order $m/\alpha$ the particles start moving until finally the Boltzmann distribution is reached. In order to illustrate the meaning of the time-dependent diffusion constant $A(t)$ we calculate the first and second cumulant with the initial distribution $g(p) = \delta(p - p_0)$. All particles have the same momentum $p_0$ at $t = 0$. In this case the first cumulant does not vanish:

$$G_\delta^{(1)} = -e^{(-\alpha/m)t} p_0 m^{-1}\cdot\frac{\partial}{\partial q}, \tag{29}$$

$$G_\delta^{(2)} = \frac{1}{\alpha}(e^{-(\alpha/m)t} - e^{-2(\alpha/m)t}) \times\left\{\frac{1}{m}\left(\frac{\partial}{\partial q}\cdot p_0\right)^2 - kT\left(\frac{\partial}{\partial q}\right)^2\right\} + \frac{1}{\alpha}(1 - e^{-(\alpha/m)t})\frac{\partial}{\partial q}\cdot\left(\frac{\partial U}{\partial q} + kT\frac{\partial}{\partial q}\right). \tag{30}$$

In the limit $t\to\infty$ both expressions (27), and (29) and (30) agree, as they should. The operator $G(t)$ is independent of the initial condition for large times. The larger $\alpha/m$, the faster $G(t)$ approaches the constant expression. For very large values of $\alpha/m$ the dynamics governed by (23) approaches a Markov process. Formally the Markovian limit is obtained by first rescaling the time $\tau = \alpha^{-1}t$ and taking the limit $\alpha\to\infty$. In this limit all higher cumulants vanish since they are proportional to higher powers of $1/\alpha$.

## III. COUPLED TRANSLATIONAL AND ROTATIONAL DIFFUSION

We consider particles of arbitrary shape in a fluid. The friction forces depend on the orientation. We will describe a proper choice for the variables. In Refs. 10 and 11 inconsistent definitions which lead to wrong results are used.

The position and orientation of each particle is determined by the six variables comprised in the sextuple $x$,

$$x = (q_1,q_2,q_3,\phi,\theta,\psi). \tag{31}$$

0 is an arbitrary origin and $C$ the center of mass. $q_1,q_2,q_3$ are the coordinates of the vector $0C$ in the laboratory frame where $\hat{e}_1,\hat{e}_2,\hat{e}_3$ are three arbitrary orthogonal vectors of length one such that $\hat{e}_1\times\hat{e}_2 = \hat{e}_3$, et cyclic. It is convenient, to choose the Euler angles $\alpha = (\phi,\theta,\psi)$ to describe the orientation.[12] We will also use the body fixed coordinate frame $\hat{e}'_1,\hat{e}'_2,\hat{e}'_3$ such that the tensor of inertia $I$ becomes diagonal. The components of the vector $\hat{e}'_i$ expressed in the laboratory fixed frame $\hat{e}_1,\hat{e}_2,\hat{e}_3$ are

$$(\hat{e}'_i)_l \equiv R_{li}(\phi,\theta,\psi),$$
$$R(\phi,\theta,\psi) \equiv [R_{li}(\phi,\theta,\psi)]. \tag{32}$$

The Euler angles are defined by

$$R(\phi,\theta,\psi) \equiv R_z(\phi)R_x(\theta)R_z(\psi). \tag{33}$$

$R_z(\phi)$ and $R_z(\psi)$ are counterclockwise rotations of a vector about the $\hat{e}_3$ axis. $R_x(\theta)$ is a rotation about the $\hat{e}_1$ axis.

$$R_z(\phi) = e^{\phi T_3},$$
$$R_x(\theta) = e^{\theta T_1}, \qquad (34)$$
$$R_z(\psi) = e^{\psi T_3}.$$

The $3\times 3$ matrices $T_1,T_2,T_3$ are defined

$$(T_i)_{lm} = \epsilon_{ilm}. \qquad (35)$$

$\epsilon_{ilm}$ is the completely antisymmetric Levi–Civita tensor. Besides the position $x$ (31) we need the momenta $y$,

$$y = (p_1', p_2', p_3', L_1', L_2', L_3'). \qquad (36)$$

Both the translational momenta $p'$ and the angular momenta $L'$ are expressed in the body fixed coordinate frame. The tensor of inertia and the friction tensor depend only on the mass distribution and shape of the particle. They are independent of the orientation if body fixed coordinates are used. According to (32) the vector $p'$ and $p \equiv m\dot{q}$, where $m$ is the mass and the dot denotes the time derivative, are related in the following way:

$$p' = R^{\dagger}(\phi,\theta,\psi)p$$
$$= R^{-1}(\phi,\theta,\psi)p. \qquad (37)$$

The angular momentum $L'$ is the product of the angular velocity $\omega'$ and the tensor of inertia $I$,

$$L' = I\omega'. \qquad (38)$$

With Eq. (37) the skewsymmetric angular velocity matrix $\Omega$ [13] expressed in the body fixed frame is

$$\Omega = R^{-1}\dot{R}. \qquad (39)$$

The matrix $\Omega$ and the pseudovector $\omega'$ are related:

$$\Omega = \sum_{i=1}^{3} \omega_i' T_i. \qquad (40)$$

In order to obtain $\Omega$ in terms of the Euler angles $\alpha = (\phi,\theta,\psi)$ and their time derivatives we substitute in (39) for the rotation $R$ the expressions (33) and (34). Evaluating the time derivative in (39) and multiplying $\dot{R}$ from the left with $R^{-1}$ leads to

$$\Omega = \dot{\phi}\, e^{-\psi T_3} e^{-\theta T_1} T_3 e^{\theta T_1} e^{\psi T_3}$$
$$+ \dot{\theta}\, e^{-\psi T_3} T_1 e^{\psi T_3} + \dot{\psi} T_3. \qquad (41)$$

We compare this expression with (40). Equation (41) can be simplified using the commutator algebra $[T_i,T_j] = \epsilon_{ijk} T_k$.[2,12] One obtains for the angular velocity $\omega'$

$$\omega_1' = \dot{\phi} \sin\theta \sin\psi + \dot{\theta}\cos\psi,$$

$$\omega_2' = \dot{\phi} \sin\theta \cos\psi - \dot{\theta}\sin\psi, \qquad (42)$$

$$\omega_3' = \dot{\psi} + \dot{\phi}\cos\theta.$$

Now we are able to describe the motion of the particle completely. The phase space $S_x \times S_y$ consists of all pairs $z = (x, y)$ defined by (31), (36), (37), (38), and (42).

### A. Liouville's equation

The motion of the rigid body is a solution of the canonical equations[8]

$$\dot{x}_c = \frac{\partial H}{\partial y_c}, \quad \dot{y}_c = -\frac{\partial H}{\partial x_c},$$
$$H(x_c, y_c) = \frac{1}{2m} ||p||^2 + \tfrac{1}{2} L'\cdot I^{-1} L' + U(x_c). \qquad (43)$$

The canonical conjugate variables $x_c$ and $y_c$ are $x_c = x$ and $y_c = (p_1, p_2, p_3, p_\phi, p_\theta, p_\psi)$. The canonical conjugate momenta for the angle variables $\alpha = (\gamma,\theta,\psi)$ are given by $p_\alpha = \partial T/\partial\dot{\alpha}$ with $T \equiv \frac{1}{2} L'\cdot I^{-1} L'$.

$$p_\phi = L_1' \sin\theta\sin\psi + L_2' \sin\theta\cos\psi + L_3' \cos\theta,$$
$$p_\theta = L_1' \cos\psi - L_2' \sin\psi, \qquad (44)$$
$$p^\psi = L_3'.$$

For every solution $z_c(t) \equiv (x_c(t), y_c(t))$ of Eq. (43) Liouville's theorem holds,

$$\frac{\partial}{\partial t} f_c(t,z_c) + \dot{z}_c \cdot \frac{\partial}{\partial z_c} f_c(t,z_c) = 0. \qquad (45)$$

It would be more convenient to express the particle density distribution $f_c$ as a function of the variables $z = (x, y)$ defined earlier, instead of as a function of $z_c = (x_c, y_c)$. We define a new density

$$f(t,z) \equiv f_c(t,z_c(z)). \qquad (46)$$

With the following identities, one obtains the Liouville equation (48) for the new density $f(t,z)$.

$$\frac{\partial}{\partial z_c} = \frac{\partial z}{\partial z_c}\frac{\partial}{\partial z},$$
$$\dot{z} = \frac{d}{dt} z(t) \equiv \frac{d}{dt} z(z_c(t)) = \frac{\partial z}{\partial z_c}\dot{z}_c, \qquad (47)$$
$$\frac{\partial z}{\partial z_c}\frac{\partial z_c}{\partial z} = \mathbb{1}_{12}$$

$\mathbb{1}_{12}$ is the 12 dimensional identity matrix. We get

$$\frac{\partial}{\partial t} f(t,z) + \dot{z}\frac{\partial}{\partial z} f(t,z) = 0. \qquad (48)$$

The transformation $z_c = z_c(z)$ is given by Eqs. (37) and (44). The Jacobian determinant is $-\sin\theta$. For any observable $O = O(z_c)$ the expectation value $EO \equiv \int dz_c O(z_c) f_c(t,z_c)$ can also be expressed in the new variables $z = (q,\alpha, p', L')$,

$$EO = \int dz \left| \operatorname{Det}\left(\frac{\partial z_c}{\partial z}\right)\right| O(z_c(z)) f(t,z)$$
$$= \int d^3q\, d\phi\, d\theta \sin\theta\, d\psi\, d^3p'\, d^3L' \qquad (49)$$
$$\times O(q,\phi,\theta,\psi, p', L') f(t,q,\phi,\theta,\psi,p',L').$$

Equations (45) and (48) are formally the same but the meaning of the differential operators $\partial/\partial z_c$ and $\partial/\partial z$ are very different.

$$\frac{\partial}{\partial z_c} = \left(\frac{\partial}{\partial x_c}, \frac{\partial}{\partial y_c}\right), \quad \frac{\partial}{\partial z} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}\right). \qquad (50)$$

The gradient $\partial/\partial x_c$ is evaluated with the canonical conjugate momenta $y_c = (p_1, p_2, p_3, p_\phi, p_\psi)$ fixed. When $\partial/\partial x$ operates, the momenta $y = (p_1', p_2', p_3', L_2', L_3')$ are fixed.

$$\frac{\partial}{\partial x^c}=\left[\left(\frac{\partial}{\partial q_1}\right)_{\substack{q_2,q_3,\phi,\theta,\psi\\ p_1,p_2,p_3,p_\phi,p_\theta,p_\psi}},\ldots,\left(\frac{\partial}{\partial\psi}\right)_{\substack{q_1,q_2,q_3,\phi,\theta\\ p_1,p_2,p_3,p_\phi,p_\theta,p_\psi}}\ldots\right],$$

$$\frac{\partial}{\partial x}=\left[\left(\frac{\partial}{\partial q_1}\right)_{\substack{q_2,q_3,\phi,\theta,\psi\\ p_1',p_2',p_3',L_1',L_2',L_3'}},\ldots,\left(\frac{\partial}{\partial\psi}\right)_{\substack{q_1,q_2,q_3,\phi,\theta\\ p_1',p_2',p_3',L_1',L_2',L_3'}}\ldots\right]. \tag{51}$$

Rather than using (47) to calculate $\dot z$ we got back to Euler's equation.

$$\frac{\partial}{\partial x_c}\mathscr{L}-\frac{d}{dt}\frac{\partial}{\partial\dot x_c}\mathscr{L}=0. \tag{52}$$

The Lagrange function $\mathscr{L}$ is $\mathscr{L}=\frac{1}{2}y^\dagger M^{-1}y-U(x_c)$. $M$ is the generalized inertia matrix

$$M=\begin{pmatrix} m\mathbf{1}_3 & 0\\ 0 & I\end{pmatrix}. \tag{53}$$

$M$ is a symmetric $6\times6$ matrix. Keeping in mind that $y=y(x_c,\dot x_c)$ Eq. (52) can be written

$$\frac{d}{dt}y^\dagger M^{-1}\frac{\partial y}{\partial\dot x_c}-y^\dagger M^{-1}\frac{\partial y}{\partial x_c}+\frac{\partial U(x_c)}{\partial x_c}=0. \tag{54}$$

The derivatives $\partial y/\partial x_c$ and $\partial y/\partial\dot x_c$ are $6\times6$ matrices. Evaluating the time derivative gives

$$\dot y^\dagger M^{-1}\frac{\partial y}{\partial\dot x_c}+y^\dagger\left(M^{-1}\frac{d}{dt}\frac{\partial y}{\partial\dot x_c}-M^{-1}\frac{\partial y}{\partial x_c}\right)+\frac{\partial U}{\partial x_c}(x_c)=0. \tag{55}$$

The following definitions are useful:

$$A_{lk}\equiv\sum_{m=1}^{6}M^{-1}_{lm}\frac{\partial y_m}{\partial\dot x_{ck}},$$

$$B_{lk}\equiv\sum_{m=1}^{6}M^{-1}_{lm}\left(\frac{d}{dt}\frac{\partial y_m}{\partial\dot x_{ck}}-\frac{\partial y_m}{\partial x_{ck}}\right). \tag{56}$$

Equation (54) can be solved for $\dot y$. The result is

$$\dot y^\dagger=-\frac{\partial U(x)}{\partial x}A^{-1}-y^\dagger BA^{-1}. \tag{57}$$

$\partial U/\partial x=\partial U/\partial x_c$ in agreement with (51) since the potential $U$ does not depend on the momenta. From the transformation $y=y(x_c,\dot x_c)$ given by (37) and (44) one obtains for the matrix $A$

$$A=\begin{pmatrix} R^{-1}(\phi,\theta,\psi) & & 0 & \\ & \sin\theta\sin\psi & \cos\psi & 0\\ 0 & \sin\theta\cos\psi & -\sin\psi & 0\\ & \cos\theta & 0 & 1\end{pmatrix}. \tag{58}$$

The inverses of this matrix is

$$A^{-1}=\begin{pmatrix} R(\phi,\theta,\psi) & & 0 & \\ & \frac{1}{\sin\theta}\sin\psi & \frac{1}{\sin\theta}\cos\psi & 0\\ 0 & \cos\psi & -\sin\psi & 0\\ & -\cot\theta\sin\psi & -\cot\theta\cos\psi & 1\end{pmatrix}. \tag{59}$$

We can write the matrix $A$ and $B$ in block form,

$$A=\begin{pmatrix} R^{-1} & 0\\ 0 & A'\end{pmatrix},\quad B=\begin{pmatrix} B_1 & B_2\\ B_3 & B_4\end{pmatrix},$$

$$BA^{-1}=\begin{pmatrix} B_1R & B_2A'^{-1}\\ B_3R & B_4A'^{-1}\end{pmatrix}. \tag{60}$$

Comparison of (37) and (44) with (58) gives

$$y=MA(x_c)\dot x_c. \tag{61}$$

With (61) the matrix $B$ can be expressed in terms of $A$. $B=(d/dt)A-(\partial/\partial x_c)A\dot x_c$. The matrix $B_1R$ is therefore equal to $((d/dt)R^{-1})R=-\Omega$. By direct calculation we find that also $B_4A'^{-1}$ is equal to $-\Omega$. The matrix $B_3$ vanishes. This leads to

$$BA^{-1}=-\begin{bmatrix}\Omega & \left(\frac{\partial}{\partial\alpha_j}\sum_{l,k}R^{-1}_{ik}\dot q_k A'^{-1}_{il}\right)\\ 0 & \Omega\end{bmatrix}. \tag{62}$$

We define the differential operator $D_x$,

$$D_x\equiv A^{-1\dagger}\frac{\partial}{\partial x}. \tag{63}$$

According to (57) $\dot y$ is

$$\dot y=-D_xU(x)+\begin{pmatrix} p'x\omega'\\ L'x\omega'\end{pmatrix}. \tag{64}$$

We used the fact that the following contribution vanishes:

$$\sum_{l,k}R^{-1}_{il}\dot q_l\frac{\partial}{\partial\alpha_j}(R^{-1}_{ik}\dot q_k)=\frac{1}{2}\sum_{l,k}\frac{\partial}{\partial\alpha_j}(R^{-1}_{il}\dot q_lR^{-1}_{ik}\dot q_k)=\frac{1}{2}\frac{\partial}{\partial\alpha_j}||R^{-1}\dot q||^2=\frac{1}{2}\frac{\partial}{\partial\alpha_j}||\dot q||^2=0.$$

Equation (64) is Euler's equation of motion for a rigid body. The differential operator $D_x$ is explicitly given by Eqs. (111) and (112). In the following it is more convenient to write the last term in Eq. (64) as a quadratic form in $y$,

$$(\dot y)_n=-(D_xU(x))_n+\sum_{l,m}a_{lmn}y_ly_m,$$

$$a_{lmn}=\tfrac{1}{2}(C^{(n)}M^{-1}+M^{-1}C^{(n)\dagger})_{lm},$$

$$C^{(n)}=\begin{pmatrix}0 & T_n\\ 0 & 0\end{pmatrix},$$

$$C^{(n+3)}=\begin{pmatrix}0 & 0\\ 0 & T_n\end{pmatrix},\quad n=1,2,3. \tag{65}$$

The tensor $a_{lmn}$ is defined such that $a_{lmn} = a_{mln}$. With these definitions we obtain Liouville's equation (48) in the form we will use it in the following.

$$\frac{\partial}{\partial t} f(t,x,y) = \Big\{ -yM^{-1}\cdot D_x + (D_x U(x))\cdot\nabla - \sum_{l,m,n} a_{lmn} y_l y_m \nabla_n \Big\} f(t,x,y). \tag{66}$$

The operator $\dot{x}\cdot\partial/\partial x$ in (48) and (51) is equal to $yM^{-1}\cdot D_x$ since $y = MA(x)\dot{x}$ [(61),(63)]. $\nabla$ denotes the gradient with respect to $y$ with components $\nabla_n \equiv \partial/\partial y_n$.

### B. Kramers–Liouville equation

The motion of the particle is influenced by an external potential $U$ and a "Brownian fluid," which is composed of molecules which exert fluctuating forces and torques,

$$\tilde{h}(t) = (\tilde{F}(t), \tilde{N}(t)). \tag{67}$$

In the absence of an external potential the equation of motion is

$$\dot{y} = -\int_{-\infty}^{t} ds\, \Gamma(t-s) y(s) + \tilde{h}(t). \tag{68}$$

For a derivation of the generalized Langevin equation (68) see Ref. 14. The friction tensor $\Gamma(t)$ is proportional to the correlation of the fluctuating forces $\tilde{h}(t)$,

$$\Gamma(t) = \frac{1}{kT} \langle \tilde{h}(0), \tilde{h}(t) \rangle. \tag{69}$$

The symmetric tensor $\Gamma(t)$ is independent of the momenta $y$ for heavy solute molecules. In the following we will use the "Markovian limit".

$$\dot{y} = -Cy + \tilde{h}(t), \quad C \equiv \int_0^\infty \Gamma(s) ds. \tag{70}$$

The following discussion can be generalized simply by replacing the $6\times 6$ matrix $C$ with the corresponding expression in (68) in all equations.

In Ref. 14, Eq. (68) was derived from a linearized set of the equation of motion. Therefore one does not have to distinguish between the laboratory and the body fixed coordinate frames. The difference consists of quadratic terms $L'\times\omega'$ and $p'\times\omega'$. The idea is that over a short time of the order of the relaxation time both frames do not differ very much. After combining the stochastic equation (70) with Newton's equation, we can follow the orbit over an arbitrary long time and must therefore distinguish between both coordinate frames. The equation of motion containing the forces due to the fluid and the external forces is

$$\dot{y} = -Cy + D_x U + \begin{pmatrix} p'\times\omega' \\ L'\times\omega' \end{pmatrix} + \tilde{h}(t) \tag{71}$$

In Refs. 10 and 11 the term $p'\times\omega'$ is omitted. The generalization of Liouville's equation including stochastic forces can be obtained from (71).[5] The result is the Kramers–Liouville equation

$$\frac{\partial}{\partial t} f = (L+K) f,$$
$$Lf = -yM^{-1}\cdot D_x f + (D_x U)\cdot\nabla f - \sum_{l,m,n} a_{lmn} y_l y_m \nabla_n f, \tag{72}$$
$$Kf = \nabla\cdot C(M^{-1}y + kT\nabla) f.$$

The operator $K$ is known as Kramers operator.

### C. The operator $\tilde{L}$

In the translational case it proved very useful to go to the "interaction picture".

$$f = e^{tK} \tilde{f},$$
$$\tilde{L}(t) \equiv e^{-tK} L e^{tK} = L + \sum_{n=1}^{\infty} [K,\cdot]^n L \left(\frac{(-t)^n}{n!}\right). \tag{73}$$

The operator $L$ consists of three terms.

$$\begin{aligned} L &= L_0 + L_f + L_q, \\ L_0 &= -y\cdot M^{-1} D_x, \\ L_f &= (D_x U)\cdot\nabla, \\ L_q &= -\sum_{lmn} a_{lmn} y_l y_m \nabla_n. \end{aligned} \tag{74}$$

The calculation of the operators $\tilde{L}_0$ and $\tilde{L}_f$ does not pose any difficulties. However, for $\tilde{L}_q$ the situation is different since $\tilde{L}_q$ contains quadratic terms in $q$. The commutators with $K$ become more complicated.

All operators needed in (74) are contained in the algebra generated by $x_i, y_m, \nabla_n, \partial/\partial x_i$. The position and momenta are independent. From the definition (51) we obtain $[\nabla_n, x_l] = 0$ and $[\partial/\partial x_i, y_m] = 0$. The partial derivative $\partial/\partial x_i$ is evaluated with the momenta $y = (p', L')$ held constant. The differential operator $(D_x)_i$ (63) also commutes with $y_m$ and $\nabla_n$ for all components $i,m,n$. The only nonvanishing commutator needed for the calculation of $\tilde{L}$ is

$$[\nabla_n, y_m] = \delta_{nm}, \quad n,m = 1,\dots,6. \tag{75}$$

The operator $\tilde{L}_0(f)$ is given by the infinite sum $\tilde{L}_0(t) = L_0 + \Sigma_{n=1}^{\infty} [K,\cdot]^n L_0((-t)^n/n!)$. In order to simplify the notation we introduce the matrices $\bar{C}$ and $\tilde{C}$ and the operator $\bar{D}_x$,

$$\bar{C} \equiv CM^{-1}, \quad \tilde{C} \equiv CkT, \quad \bar{D}_x \equiv -M^{-1} D_x. \tag{76}$$

Kramers operator becomes

$$K = \nabla\cdot\bar{C}y + \nabla\cdot\tilde{C}\nabla. \tag{77}$$

The operator $L_0$ is $L_0 = y\cdot\bar{D}_x$. The first time-dependent term in the expression for $\tilde{L}_0(t)$ is equal to $-t[K, L_0]$. This commutator is

$$\begin{aligned} [K, L_0] &= [\nabla\cdot\bar{C}y, y\cdot\bar{D}_x] + [\nabla\cdot\tilde{C}\nabla, y\cdot\bar{D}_x] \\ &= \sum_{n,l,m} \bar{C}_{nl} (\bar{D}_x)_m [\nabla_n y_l, y_m] \\ &\quad + \sum_{n,l,m} \tilde{C}_{nl} (\bar{D}_x)_m [\nabla_n \nabla_l, y_m]. \end{aligned} \tag{78}$$

The following identities hold for arbitrary operators $A,B,C$:

$$\begin{aligned} [A, BC] &= [A,B]C + B[A,C], \\ [AB, C] &= A[B,C] + [A,C]B. \end{aligned} \tag{79}$$

With (79), (78) becomes

$$[K,L_0] = \sum_{n,l,m} \bar{C}_{nl}(\bar{D}_x)_m \{\nabla_n [y_l, y_m] + [\nabla_n, y_m] y_l\}$$
$$+ \sum_{n,l,m} \tilde{C}_{nl}(\bar{D}_x)_m \{\nabla_n [\nabla_l, y_m] + [\nabla_n, y_m]\nabla_l\}.$$

With (75) and using the fact that the matrix $\tilde{C} = CkT$ is symmetric,[14] leads to

$$[K,L_0] = \bar{D}_x \cdot \bar{C}y + 2\bar{D}_x \cdot \tilde{C}\nabla. \tag{80}$$

For the higher order commutators one obtains

$$[K,\cdot]^n L_0 = \bar{D}_x \cdot \bar{C}^n y + 2 \sum_{m+l=n-1} \bar{D}_x \cdot \bar{C}^m \tilde{C}(-\bar{C}^\dagger)^l \nabla. \tag{81}$$

This equation can be proved by induction on $n$. The calculation is similar to the calculation of $[K,L_0]$. We observe that the matrix $\bar{C}^m\tilde{C}$ is symmetric for all $m \geqslant 0$ since

$$\bar{C}^m \tilde{C} = CM^{-1}CM^{-1} \cdots CM^{-1}CkT$$
$$= (\bar{C}^m \tilde{C})^\dagger = \tilde{C}\bar{C}^{\dagger m}.$$

$C$ and $M$ are symmetric. Using this property the last term in (81) becomes $2\Sigma_{m+l=n-1} \bar{D}_x \cdot \bar{C}^m (\bar{C})^l \tilde{C}\nabla$. The sum vanished for even $n$. For odd $n$ it is equal to $2\bar{D}_x \cdot \bar{C}^{n-1}\tilde{C}\nabla$.

$$[K,\cdot]^n L_0 = \begin{cases} \bar{D}_x \cdot \bar{C}^n y, & n \text{ even} \\ \bar{D}_x \cdot \bar{C}^n y + 2\bar{D}_x \cdot \bar{C}^{n-1}\tilde{C}\nabla, & n \text{ odd.} \end{cases} \tag{82}$$

The final result for the operator $\bar{L}_0(t)$ is

$$\tilde{L}_0(t) = \sum_{n=0}^{\infty} [K,\cdot]^n L_0 [(-t)^n/n!]$$
$$= \bar{D}_x \cdot e^{-t\bar{C}} y + \bar{D}_x \cdot (e^{t\bar{C}} - e^{-t\bar{C}})\, \bar{C}^{-1}\tilde{C}\nabla, \tag{83}$$

and with the definitions of $\bar{C}$, $\tilde{C}$, and $\bar{D}_x$ [(76)] one obtains

$$\tilde{L}_0(t) = -y \cdot M^{-1}E(-t)D_x$$
$$+ kT\nabla \cdot [E(t) - E(-t)]D_x. \tag{84}$$

The matrix $E(t)$ is the exponential

$$E(t) \equiv e^{tCM^{-1}}. \tag{85}$$

The corresponding expression used earlier for the translational motion

$$\frac{-p}{m} \cdot \frac{\partial}{\partial q} e^{-(\alpha/m)t} + 2kT \sinh\left(\frac{\alpha}{m} t\right) \frac{\partial}{\partial p} \cdot \frac{\partial}{\partial q}$$

is a special case of (84). It is remarkable that no higher than second order derivatives appear in $\tilde{L}_0(t)$!

The calculation of the operator $\tilde{L}_f$ is similar. One obtains

$$\tilde{L}_f(t) = \nabla \cdot E(t)[D_x U(x)]. \tag{86}$$

In the final step we calculate the operator $\tilde{L}_q$ which is quadratic in the momenta $y$. This leads to major complications, but it turns out that the operator $\tilde{L}_q(t)$ contains no higher order derivatives than a third order derivative in the momenta $q$.

We will write $L_q$ as the scalar product of two vectors with $6^3 = 216$ components [(74)]:

$$L_q \equiv -a \cdot (y \otimes y \otimes \nabla). \tag{87}$$

In order to find the commutators $[K,\cdot]^n L_q$ we make the ansatz that there exist some vectors $W^{(n)}, X^{(n)}, Y^{(n)}, Z^{(n)}$ such that

$$[K,\cdot]^n L_q = W^{(n)} \cdot (y \otimes y \otimes \nabla) + X^{(n)*} \cdot \nabla$$
$$+ Y^{(n)}(y \otimes \nabla \otimes \nabla) + Z^{(n)} \cdot (\nabla \otimes \nabla \otimes \nabla). \tag{88}$$

The vector $X^{(n)*} \in \mathbb{R}^6$ is defined $X_k^{(n)*} \equiv \Sigma_l X_{llk}^{(n)}$. The definition of the $n$th commutator [(16)] $[K,\cdot]^n L_q = [K,\cdot]([K,\cdot]^{n-1}L_q)$ allows us to derive recursion relations for the vectors $W^{(n)}$, $X^{(n)}$, $Y^{(n)}$, $Z^{(n)}$.

*Lemma*: $W^{(0)} = -a$, $X^{(0)} = 0$, $Y^{(0)} = 0$, $Z^{(0)} = 0$,

$$W^{(n+1)} = W^{(n)}\Sigma$$
$$X^{(n+1)} = X^{(n)}\Omega + W^{(n)}\Xi$$
$$Y^{(n+1)} = Y^{(n)}\Upsilon + W^{(n)}\Psi \tag{89}$$
$$Z^{(n+1)} = Z^{(n)}\Phi + W^{(n)}\Xi$$

The $216 \times 216$ matrices $\Upsilon, \Phi, \Xi, \Psi, \Sigma$ are defined

$$\Sigma = \bar{C} \otimes \mathbb{1} \otimes \mathbb{1} + \mathbb{1} \otimes \bar{C} \otimes \mathbb{1} - \mathbb{1} \otimes \mathbb{1} \otimes \bar{C}^\dagger,$$
$$\Upsilon = \bar{C} \otimes \mathbb{1} \otimes \mathbb{1} - \mathbb{1} \otimes \bar{C}^\dagger \otimes \mathbb{1} - \mathbb{1} \otimes \mathbb{1} \otimes \bar{C}^\dagger,$$
$$\Phi = -\bar{C}^\dagger \otimes \mathbb{1} \otimes \mathbb{1} - \mathbb{1} \otimes \bar{C}^\dagger \otimes \mathbb{1} - \mathbb{1} \otimes \mathbb{1} \otimes \bar{C}^\dagger, \tag{90}$$
$$\Xi = 2\tilde{C} \otimes \mathbb{1} \otimes \mathbb{1},$$
$$\Psi = 4\mathbb{1} \otimes \tilde{C} \otimes \mathbb{1},$$
$$\Omega = -\mathbb{1} \otimes \mathbb{1} \otimes \bar{C}^\dagger.$$

$\mathbb{1}$ is the $6 \times 6$ identity matrix. $W_{klm}^{(n)}$ is symmetric in the first two indices $W_{klm}^{(n)} = W_{lkm}^{(n)}$ for all $n = 0,1,2,\ldots$.

*Proof*: All these relations follow directly from the definition of $X^{(n)}, Y^{(n)}, W^{(n)}, Z^{(n)}$ [(88)] and the definition of the commutator $[K,\cdot]^n$[(16)].

The following equations are true for arbitrary vectors $X^{(n)}, Y^{(n)}, W^{(n)}, Z^{(n)}$ with the only restriction that $W^{(n)}$ is symmetric in the first two indices.

$$W_{klm}^{(n)} = W_{lkm}^{(n)}. \tag{91}$$

(1) $[\nabla \cdot \bar{C}y, X^{(n)*} \cdot \nabla] = (X^{(n)}\Omega)^* \cdot \nabla$,

(2) $[\nabla \cdot \bar{C}y, W^{(n)} \cdot (y \otimes y \otimes \nabla)] = W^{(n)}\Sigma \cdot (y \otimes y \otimes \nabla)$,

(3) $[\nabla \cdot \bar{C}y, Y^{(n)} \cdot (y \otimes \nabla \otimes \nabla)] = Y^{(n)}\Upsilon \cdot (y \otimes \nabla \otimes \nabla)$,

(4) $[\nabla \cdot \bar{C}y, Z^{(n)} \cdot (\nabla \oplus \nabla \oplus \nabla)] = Z^{(n)}\Phi \cdot (\nabla \otimes \nabla \oplus \nabla)$, (92)

(5)
$[\nabla \cdot \tilde{C}\nabla, W^{(n)} \cdot (y \otimes y \otimes \nabla)] = (W^{(n)}\Xi)^* \cdot \nabla + W^{(n)}\Psi \cdot (y \otimes \nabla \otimes \nabla)$,

(6) $[\nabla \cdot \tilde{C}\nabla, Y^{(n)} \cdot (y \otimes \nabla \otimes \nabla)] = Y^{(n)}\Xi \cdot (\nabla \oplus \nabla \otimes \nabla)$,

(7) $[\nabla \cdot \tilde{C}\nabla, Z^{(n)} \cdot (\nabla \otimes \nabla \otimes \nabla)] = 0$.

The proof of these equations is mostly straightforward. For instance, the first equation is

$$[\nabla \cdot \bar{C}y, X^{(n)*} \cdot \nabla] = \sum_{\alpha,\beta,\gamma} \bar{C}_{\alpha\beta} X_\gamma^{(n)*} [\nabla_\alpha y_\beta, \nabla_y]$$
$$= \sum_{\alpha,\beta,\gamma} \bar{C}_{\alpha\beta} X_\gamma^{(n)*} \nabla_\alpha (-\delta_{\alpha\beta}) = X^{(n)*}(-\bar{C}^\dagger) \cdot \nabla$$
$$= (X^{(n)})^* \cdot \nabla.$$

The fifth equation is different since there are two different types of terms:

$$[\nabla\cdot\tilde{C}\nabla, W^{(n)}\cdot(y\otimes y\otimes\nabla)]$$
$$= \sum_{\alpha,\beta,\gamma,\delta,\epsilon} \tilde{C}_{\alpha\beta} W^{(n)}_{\gamma\delta\epsilon}\{(\nabla_\alpha[\nabla_\beta, y_\gamma] + y_\delta\nabla_\epsilon) + [\nabla_\alpha, y_\gamma]\nabla_\beta y_\delta\nabla_\epsilon + y_\gamma\nabla_\alpha[\nabla_\beta, y_\delta]\nabla_\epsilon + y_\gamma[\nabla_\alpha, y_\delta]\nabla_\beta\nabla_\epsilon\}.$$

By assumption $W^{(n)}_{\gamma\delta\epsilon} = W^{(n)}_{\delta\gamma\epsilon}$ and $[y_\alpha, \nabla_\beta] = -\delta_{\alpha\beta}$. This gives the result

$$[\nabla\cdot\tilde{C}\nabla, W^{(n)}\cdot(y\otimes y\otimes\nabla)] = (W^{(n)}\Xi)^*\cdot\nabla + W^{(n)}\Psi\cdot(y\otimes\nabla\otimes\nabla).$$

The proof of the other equations is similar.

We define the vector valued function $W(t):\mathbb{R}\rightarrow\mathbb{R}^{216}$,

$$W(t) \equiv \sum_{n=0}^{\infty} ((-t)^n/n!) W^{(n)} \tag{93}$$

and similarly $X^*(t)$, $Y(t)$, and $Z(t)$. The recursion relations (89) for $W^{(n)}$, $X^{*(n)}$, $Y^{(n)}$, and $Z^{(n)}$ lead to the differential equations

$$\begin{aligned} &W(0) = -a, \quad X(0) = 0, \quad Y(0) = 0, \quad Z(0) = 0,\\ &\dot{W}(t) = -W(t)\Sigma,\\ &\dot{X}(t) = -X(t)\Omega - W(t)\Xi,\\ &\dot{Y}(t) = -Y(t)\Upsilon - W(t)\Psi,\\ &\dot{Z}(t) = -Z(t)\phi - Y(t)\Xi. \end{aligned} \tag{94}$$

These differential equations can be integrated and the results are

$$\begin{aligned} &W(t) = -a\exp(-t\Sigma),\\ &X(t) = a\int_0^t ds \exp(-s\Sigma)\Xi\exp([s-t]\Omega),\\ &Y(t) = a\int_0^t ds\exp(-s\Sigma)\Psi\exp([s-t]\Upsilon),\\ &Z(t) = -\int_0^t ds Y(s)\Xi\exp([s-t]\Phi). \end{aligned} \tag{95}$$

With these expressions the final result for the operator $\tilde{L}(t)$ is with (84), (86), (88), (95):

$$\begin{aligned} \tilde{L}(t) = &-y\cdot M^{-1}E(t)D_x\\ &+ kT\nabla\cdot[E(t) - E(-t)]D_x\\ &+ \nabla\cdot E(t)[D_x U(x)]\\ &+ W(t)\cdot(y\otimes y\otimes\nabla) + X^*(t)\cdot\nabla\\ &+ Y(t)\cdot(y\otimes\nabla\otimes\nabla) + Z(t)\cdot(\nabla\otimes\nabla\otimes\nabla). \end{aligned} \tag{96}$$

This is the Liouville operator in the interaction picture. The quadratic term $L_q$ caused all the additional terms. Even if they are not explicitly known, we will be able to show that they do not contribute to the first and second cumulants.

### D. First cumulant

We calculate the cumulants under the assumption that initially the distribution in the momenta $y$ is a Maxwell distribution,

$$g(y) = \frac{1}{(2\pi kT)^3(\det M)^{1/2}} e^{-y\cdot M^{-1}y/2kT}. \tag{97}$$

The first cumulant is according to (25)

$$G^{(1)}(t) = \int d^6y\,\tilde{L}(t)\,g(y). \tag{98}$$

We use expression (96) of $\tilde{L}(t)$ and integrate by parts. The contribution at the boundaries vanish. The remaining terms are integrals over odd functions in $y_m$, which vanish. The first cumulant is identically zero for all times $t\geqslant 0$,

$$G^{(1)}(t)P(t,x) = 0. \tag{99}$$

### E. Second cumulant

The second cumulant gives the first nonvanishing contribution,

$$G^{(2)}(t) = \int_0^t ds\int d^6y\,\tilde{L}(t)\,\tilde{L}(s)\,g(y) \tag{100}$$

with [(96)]

$$\begin{aligned} G^{(2)}(t) = &-\int_0^t ds\int d^6y\,y\cdot M^{-1}E(-t)\,D_x\\ &\times[-y\cdot M^{-1}E(-s)D_x\\ &+ kT\nabla\cdot\{E(s) - E(-s)\}D_x\\ &+ \nabla\cdot E(s)[D_x U(x)] + W(s)\cdot(y\otimes y\otimes\nabla)\\ &+ X^*(s)\cdot\nabla + Y(s)\cdot(y\otimes\nabla\otimes\nabla)]g(y). \end{aligned} \tag{101}$$

The remaining terms of the product $\tilde{L}(t)\tilde{L}(s)$ vanish after integrating by parts. The only term left from the operator $\tilde{L}(t)$ is $-y\cdot M^{-1}E(-t)D_x$. Also the term $Z(s)\cdot(\nabla\otimes\nabla\otimes\nabla)$ vanished after integrating by parts three times.

At first we can show that the contribution due to the terms $W(s)\cdot(y\otimes y\otimes\nabla)$, $X^*(s)\cdot\nabla$, and $Y(s)\cdot(y\otimes\nabla\otimes\nabla)$ cancel each other. We will show that the following integral vanishes for $k = 1,2,\ldots,6$ and all times $s\geqslant 0$:

$$J_k^{(s)} = \int d^6y\,y_k\,[W(s)\cdot(y\otimes y\otimes\nabla) + X^*(s)\cdot\nabla + Y(s)\cdot(y\otimes\nabla\otimes\nabla)]g(y). \tag{102}$$

We recall that $\int d^6y\,y_i\,y_j\,g(y) = M_{ij}kT$. Again integrating by parts (102) becomes

$$J_k(s) = -\sum_{n,m}(kTW_{nmk}(s)M_{nm} + X_{nnk}(s) - Y_{nnk}(s)). \tag{103}$$

The function $J_k(s)$ may be written as $J_k(s) = \Sigma_{n=0}^{\infty} J_k^{(n)}(-s)^n/n!$. For the constants $J_k^{(n)}$ one obtains, according to (93),

$$J_k^{(l)} = -\sum_{n,m}(kTW^{(l)}_{nmk}M_{nm} + X^{(l)}_{nnk} - Y^{(l)}_{nnk}). \tag{104}$$

The recursion relations (89) allow us to define $J_k^{(l)}$ in terms of $J_k^{(l-1)}$,

$$J_k^{(l)} = \sum_{l',k',m'}\Big(kTW^{(l-1)}_{k'l'm'}M_{k'l'}\bar{C}^\dagger_{m'k} + X^{(l-1)}_{k'k'm'}\bar{C}_{m'k} + Y^{(l-1)}_{k'k'm'}\bar{C}^\dagger_{m'k}\Big).$$

Comparing this expression with (103) shows

$$J_k^{(l)} = -\sum_{k'} J_{k'}^{(l-1)} \bar{C}^{\dagger}_{k'k} = (J^{(l-1)}\bar{C}^{\dagger})_k. \qquad (106)$$

The vector $J_k^{(0)}$ vanishes because $X^{(0)} = y^{(0)} = 0$ and $\Sigma_{k'l'} W^{(0)}_{k'l'm} M_{k'l'} = -\Sigma_{k'l'} a_{k'l'm} M_{k'l'}$

$= -\frac{1}{2}\,\mathrm{Tr}(C^{(m)} + M^{-1}C^{(m)\dagger}M) = 0$ [(65), (89)]. This shows that $J_k^{(l)} = 0$ for all $l$ and $k$. Therefore

$$J_k(s) = 0, \quad s \geqslant 0. \qquad (107)$$

The integration of the remaining four terms in (101) is straightforward. One has to keep in mind that the matrix $M^{-1}E(t)$ is symmetric.

The final result is

$$\frac{d}{dt} P(t,x) \cong G^{(2)}(t) P(t,x)$$

$$= D_x \cdot \Lambda(t)\left(D_x + \frac{1}{kT}(D_x U(x))\right)P(t,x). \qquad (108)$$

The time-dependent diffusion matrix is

$$\Lambda(t) = kTC^{-1}(1 - e^{-tCM^{-1}}), \quad t \geqslant 0. \qquad (109)$$

Equation (108) is the generalized Smoluchowski equation for coupled translational and rotational diffusion. Since we started with a Maxwell distribution at $t = 0$, the diffusion matrix $\Lambda(t)$ is time dependent. Equation (108) includes as a special case the translational diffusion and the rotational diffusion discussed in Ref. 1. The operator $D_x$ depends on the orientation $\alpha = (\phi,\theta,\psi)$.

$$D_x \equiv \begin{pmatrix} D_{q'} \\ D_\alpha \end{pmatrix}, \qquad (110)$$

$$D_{q'} = R^{\dagger}(\phi,\theta,\psi) \begin{pmatrix} \partial/\partial q_1 \\ \partial/\partial q_2 \\ \partial/\partial q_3 \end{pmatrix}, \qquad (111)$$

$$D_\alpha = \begin{pmatrix} \cos\psi \dfrac{\partial}{\partial\theta} + \sin\psi \dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\phi} - \cot\theta \sin\psi \dfrac{\partial}{\partial\psi} \\ -\sin\psi \dfrac{\partial}{\partial\theta} + \cos\psi \dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\phi} - \cot\theta\cos\psi \dfrac{\partial}{\partial\psi} \\ \dfrac{\partial}{\partial\psi} \end{pmatrix}. \qquad (112)$$

The rotation $R(\phi,\theta,\psi)$ is defined in (33) and (34). The expression for $D_\alpha$ follows from (59) and (63). Usually the friction tensor $C$ is split into four $3\times 3$ matrices.

$$C = \begin{pmatrix} C_{TT} & C_{TR} \\ C_{RT} & C_{RR} \end{pmatrix}. \qquad (113)$$

For axialsymmetric molecules it is easy to show that $C_{TR} = C_{RT} = 0$.[8] In this case the diffusion equation is

$$\frac{\partial}{\partial t} P(t,q,\alpha) = \Big\{ D_{q'} \cdot \Lambda_T\Big(D_{q'} + \frac{1}{kT}[D_{q'} U(q,\alpha)]\Big) \qquad (114)$$

$$+ D_\alpha \cdot \Lambda_r\Big(D_\alpha + \frac{1}{kT}[D_\alpha U(q,\alpha)]\Big)\Big\} P(t,q,\alpha),$$

with

$$\Lambda_t = kTC_{TT}^{-1}(1 - e^{-tC_{TT}m^{-1}}),$$

$$\Lambda_R = kTC_{RR}^{-1}(1 - e^{-tC_{RR}I^{-1}}), \quad t \geqslant 0.$$

The diffusion of translational and rotational degrees of freedom is still coupled even if the potential $U$ vanishes, since $D_{q'}$, depends on $\alpha$. In Sec. V we will solve (114) in two dimensions for $U(q,\alpha) = 0$.

In Refs. 10 and 11, different expressions for the operators corresponding to $D_{q'}$ and $D_\alpha$, which are wrong in our opinion, are used. Instead of $D_\alpha$ the operator $J \equiv -iqx(\partial/\partial q)$ was used. $J$ is, up to a constant factor, the quantum mechanical angular momentum operator for a rotating *point particle*. Both operators $D_\alpha$ and $J$ have the same commutator algebra since they are both infinitesimal generators of a representation of SO(3). $D_\alpha$ and $J$ correspond to two different representations; see (136). A connection between $J = -iqx(\partial/\partial q)$ and the three Euler angles $(\phi,\theta,\psi)$ also used in Refs. 10 and 11 is not obvious.

For axially symmetric particles one can factorize the angular dependence of $P(t,q,\phi,\theta,\psi)$ in $\psi$. The operator $D_\alpha^2$ is in general not equal to $\Delta\,|_{r=1}$, the Laplace operator in spherical coordinates on the unit sphere. This is only true if we set $\partial/\partial\psi = 0$. If we consider only axial symmetric molecules and do not distinguish between two orientations which differ only by a rotation about the axis of symmetry, then we may use $D_\alpha^2\,|_\psi = \Delta\,|_{r=1}$; see (136). Reference 10 obtained wrong results by setting $J^2 = \Delta$.

It is important to keep in mind that the operator $D_{q'}$ depends on the orientation. $D_{q'}$ is the gradient along the body fixed coordinate axis. If $D_{q'}$ is replaced by $D_q = \partial/\partial q$ one obtains wrong results.[10,11] The coupling of translational and rotational diffusion of the two dimensional model discussed in Sec. V is a consequence of the $\alpha$ dependence of $D_{q'}$, only.

These claims will be justified in detail in Sec. V.

## IV. *N* PARTICLE DIFFUSION

We consider $N$ particles moving in a fluid interacting via arbitrary forces. In general the $N$ particle density $P(t,x^{(1)},x^{(2)},\ldots,x^{(N)})$ is not the product of the distributions $P(t,x^{(i)})$, where $x^{(i)}$ denotes the six coordinates of the $i$th particle $x^{(i)} = (q^{(1)},\alpha^{(i)})$. The $N$ particles are correlated. The interaction energy is

$$U(x^{(1)},x^{(2)},\ldots,x^{(N)}).$$

For an arbitrary observable $O(x^{(1)},x^{(2)},\ldots,x^{(N)})$ depending on the position and orientation of the particles $1,\ldots,N$ the expectation value is defined

$$EO(t) \equiv \int d\mu_{\mathbf{x}} P(t,\mathbf{x}) O(\mathbf{x}) \qquad (115)$$

with $\mathbf{x} \equiv (x^{(1)},x^{(2)},\ldots,x^{(N)})$. The volume element $d\mu_{\mathbf{x}}$ is the product measure

$$d\mu_{\mathbf{x}} = \prod_{i=1}^{N} dq_1^{(i)} dq_2^{(i)} dq_3^{(i)} d\phi^{(i)} \sin\theta^{(i)} d\theta^{(i)} d\psi^{(i)}. \qquad (116)$$

The objectives of this section is to derive the evolution equation for the $N$ particle density $P(t,\mathbf{x})$ based on the Kramers–Liouville equation for the $N$ particle motion. For the complete description of the $N$ particle dynamics all positions $x^{(i)}$ and all momenta $y^{(i)}$ are required.

$$z^{(i)}\equiv(x^{(i)},y^{(i)}),$$
$$\mathbf{z}(t)\equiv(z^{(1)}(t),z^{(2)}(t),\ldots,z^{(N)}(t)). \tag{117}$$

These variables are connected with the canonical variables $\mathbf{z}_c(t)$ through the transformation (37) and (44) applied on every single coordinate $z^{(i)}$, $i=1,\ldots,N$,

$$\mathbf{z}(t)=\mathbf{z}(\mathbf{z}_c(t))\equiv[z^{(1)}(z_c^{(1)}(t)),\ldots,z^{(N)}(z_c^{(N)}(t))]. \tag{118}$$

Liouville's equation holds for the density $f_c(t,\mathbf{z}_c)$ since the determinant of the Jacobian matrix of the flux $\mathbf{z}_c(t)$ is equal to 1 as a consequence of Hamilton's equation.

$$(\dot{x}_c^{(i)})_k=\frac{\partial H}{\partial(y_c^{(i)})_k},\quad (\dot{y}_c^{(i)})_k=-\frac{\partial H}{\partial(x_c^{(i)})_k} \tag{119}$$

for $k=1,2,\ldots,6$ and $i=1,2,\ldots,N$. The Hamiltonian function is

$$H(\mathbf{x},\mathbf{y})=\frac{1}{2}\sum_{i=1}^{N}y^{(i)}\cdot M^{(i)-1}y^{(i)}+U(x^{(1)},\ldots,x^{(N)}).$$

The matrix $M^{(i)}$ is the generalized inertia matrix (53) of the $i$th particle. Liouville's equation is

$$\frac{\partial}{\partial t}f_c(t,\mathbf{z}_c)+\dot{\mathbf{z}}_c\cdot\frac{\partial}{\partial\mathbf{z}_c}f_c(t,\mathbf{z}_c)=0. \tag{120}$$

$\dot{\mathbf{z}}_c$ is determined by (119). The expectation value of an observable $O(\mathbf{z}_c)$ is obtained by

$$EO(t)=\int d\mu_c\,f_c(t,\mathbf{z}_c)O(\mathbf{z}_c) \tag{121}$$

$d\mu_c$ is the volume element in the phase space $(S_{x_c}\times S_{y_c})^{xN}$.

$$d\mu_c=\prod_{i=1}^{N}\prod_{k=1}^{12}d(z_c^{(i)})_k. \tag{122}$$

Instead of the canonical variables $\mathbf{z}_c$ we use again $\mathbf{z}$. The transformation of the density $f_c$, the observable 0, and the measure $d\mu_c$ are

$$f(t,\mathbf{z})\equiv f_c(t,\mathbf{z}_c(\mathbf{z})),$$
$$O(\mathbf{z})\equiv O(\mathbf{z}_c(\mathbf{z})),$$
$$d\mu\equiv\left|\operatorname{Det}\frac{\partial\mathbf{z}_c}{\partial\mathbf{z}}\right|dz$$
$$=\prod_{i=1}^{N}\sin\theta^{(i)}\prod_{k=1}^{12}dz_k^{(i)}. \tag{123}$$

The expectation value of the function $O(\mathbf{z})$,

$$EO(t)=\int d\mu\,f(t,\mathbf{z})O(\mathbf{z}), \tag{124}$$

agrees with the definition (121).

The Kramers–Liouville equation for the $N$ particle problem has the form

$$\frac{\partial}{\partial t}f(t,\mathbf{z})=-\dot{\mathbf{z}}\cdot\frac{\partial}{\partial\mathbf{z}}f(t,\mathbf{z})+\sum_{i=1}^{N}K^{(i)}f(t,\mathbf{z}). \tag{125}$$

$K^{(i)}$ is the Kramers operator acting on the $i$th particle,

$$K^{(i)}\equiv\nabla^{(i)}\cdot C^{(i)}[M^{(i)-1}y^{(i)}+kT\nabla^{(i)}],$$
$$\nabla^{(i)}\equiv\frac{\partial}{\partial y^{(i)}}. \tag{126}$$

The Kramers operator is the direct sum of the individual operators $K^{(i)}$ acting on the $i$th particle. The forces due to the fluid are completely random and not correlated at different positions.[14] The correlation matrix of all components of all random forces and random torques, which is a $6^N\times6^N$ matrix, is the direct sum of the correlation matrices $C^{(i)}$. Therefore Eq. (126) is justified. With $L^{(i)}$, the Liouville operator acting on the $i$th particle, the Kramers–Liouville equation (125) is the sum of $N$ formally identical operators,

$$\frac{\partial}{\partial t}f(t,\mathbf{z})=\sum_{i=1}^{N}(L^{(i)}+K^{(i)})f(t,\mathbf{z}),$$
$$L^{(i)}=-y^{(i)}\cdot M^{(i)-1}D_{x(i)}+D_{x(i)}U(\mathbf{x})\cdot\nabla^{(i)}$$
$$-a^{(i)}\cdot(y^{(i)}\oplus y^{(i)}\otimes\nabla^{(i)}). \tag{127}$$

All operators $L^{(i)}$ are connected through the potential $U(\mathbf{x})$. Equation (127) contains the complete $N$ body dynamics.

Since $[K^{(i)},L^{(i)}]=0$ for $i\neq j$ we have

$$\exp\Big(-t\sum_{i=1}^{N}K^{(i)}\Big)\sum_{j=1}^{N}L^{(j)}\exp\Big(t\sum_{i=1}^{N}K^{(i)}\Big)$$
$$=\sum_{i=1}^{N}e^{-tK^{(i)}}L^{(i)}e^{tK^{(i)}}$$
$$=\sum_{i=1}^{N}\tilde{L}^{(i)}(t). \tag{128}$$

The operator $\tilde{L}^{(i)}(t)$ are given in Eq. (96) after replacing $z$ by $z^{(i)}$, and $M$ by $M^{(i)}$. The evolution equation for the density $\tilde{f}$ defined by $f\equiv e^{tK}\tilde{f}$ is therefore

$$\frac{\partial}{\partial t}\tilde{f}(t,\mathbf{z})=\sum_{i=1}^{N}\tilde{L}^{(i)}(t)\tilde{f}(t,\mathbf{z}). \tag{129}$$

Suppose the momentum distribution is Gaussian initially,

$$g(\mathbf{y})=\prod_{i=1}^{N}g(y^{(i)}),$$
$$g(y^{(i)})=\frac{1}{(2\pi kT)^3(\det M)^{1/2}}e^{-y^{(i)}\cdot M^{(i)-1}y^{(i)}/2kT}. \tag{130}$$

As in the one particle case the first cumulant vanishes.

$$G^{(1)}(t)P(t,\mathbf{z})=\int\prod_{i=1}^{N}d^6y^{(i)}\sum_{j=1}^{N}\tilde{L}^{(j)}(t)\prod_{k=1}^{N}g(y^{(k)})P(t,\mathbf{x})$$
$$=\sum_{j=1}^{N}\int d^6y^{(j)}\tilde{L}^{(j)}(t)g(y^{(j)})P(t,\mathbf{x})=0. \tag{131}$$

The second cumulant is

$$G^{(2)}(t)P(t,\mathbf{x}) = \int_0^t ds \int \prod_{i=1}^{N} d^6y^{(i)} \sum_{l=1}^{N}\sum_{m=1}^{N} \widetilde{L}^{(l)}(t)\widetilde{L}^{(m)}(s) \prod_{j=1}^{N} g(y^{(j)})\, P(t,\mathbf{x})$$

$$= \int_0^t ds \sum_{l=1}^{N} \int \prod_{i=1}^{N} d^6y^{(i)}\widetilde{L}^{(l)}(t)\widetilde{L}^{(l)}(s) \prod_{j=1}^{N} g(y^{(j)})P(t,\mathbf{x})$$

$$+ \int_0^t ds \sum_{l\neq m} \int \prod_{i=1}^{N} d^6y^{(i)}\widetilde{L}^{(l)}(t)\widetilde{L}^{(m)}(s) \prod_{j=1}^{N} g(y^{(j)})P(t,\mathbf{x})$$

$$= \left\{ \sum_{l=1}^{N} G^{(2)(l)}(t) + \sum_{l\neq m} \int_0^t ds\, G^{(1)(l)}(t)\, G^{(1)(m)}(s) \right\} P(t,\mathbf{x}). \qquad (132)$$

The second term vanishes because all first cumulants $G^{(1)(l)}$ $l = 1,\dots,N$ are zero. The remaining term is the sum of the cumulants calculated for the one particle dynamics. The $N$ particle diffusion equation is

$$\frac{\partial}{\partial t} P(t,x^{(1)},\dots,x^{(N)}) = \sum_{i=1}^{N} D_{x(i)}\cdot\Lambda^{(i)}(t) \times\left(D_{x(i)} + \frac{1}{kT} D_{x(i)}\, U(x^{(1)},\dots,x^{(N)})\right) \times P(t,x^{(1)},\dots,x^{(N)}),$$

$$\Lambda^{(i)}(t) = kTC^{(i)-1}(\mathbb{1} - e^{-tC_{(i)}M^{(i)-1}}). \qquad (133)$$

This is the generalization of the Smoluchowski equation for $N$ interacting translating and rotating particles.

## V. CORRELATIONS BETWEEN THE VARIABLES $q$ AND $\alpha$

We consider the one particle diffusion equation (114). In general the positions and orientations are correlated. The correlations are not only caused by the potential $U = U(x)$, $x = (q,\alpha)$ or by nonvanishing elements of the matrix $C_{TR} = C^{\dagger}_{RT}$. We will show that, if the positions $q$ and the orientations $\alpha$ are uncorrelated at $t = t_0$ there are in general correlations for $t > t_0$ even if the potential vanishes and also $C_{TR} = 0$.

### A. Axially symmetric particles

As an illustration we consider axially symmetric particles. In this case one can show that $C_{TR} = 0$.[15] If we identify the axis of symmetry with the $e'_3$ axis the matrices $C^{-1}_{TT}$ and $C^{-1}_{RR}$ are diagonal.

$$C^{-1}_{TT} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a_3 \end{pmatrix}, \quad C^{-1}_{RR} = \begin{pmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b_3 \end{pmatrix}. \qquad (134)$$

We assume that we know the distribution at time $t = t_0$, where $t_0$ is large compared with the translational and rotational relaxation time of the momenta.

$$t_0 \gg m\,||C^{-1}_{TT}|| \text{ and } t_0 \gg ||C^{-1}_{RR} I\,||,$$

$$\frac{\partial}{\partial t} P(t,q,\alpha) = kT\,[aD^2_{q'} + (a_3 - a)(D_{q'})^2_3 + bD^2_{\alpha} + (b_3 - b)(D_{\alpha})^2_3\,]P(t,q,\alpha) \quad \text{for } t > t_0. \qquad (135)$$

This equation is a special case of (114) where we used expression (134) for the friction tensor. We also used $\Lambda(t) \cong kTC^{-1}$ for $t \geqslant t_0$.

The differential operators $(D_{q'})^2$, $(D_{q'})^2_3$, $D^2_{\alpha}$, and $(D_{\alpha})^2_3$ are given by Eqs. (111) and (112).

$$(D_{q'})^2 = \Delta_q,$$

$$(D_{q'})^2_3 = \frac{\partial}{\partial q}\cdot B(\alpha)\frac{\partial}{\partial q}; \quad B_{ij}(\alpha) \equiv R_{3i}(\alpha)R_{3j}(\alpha),$$

$$(D_{\alpha})^2 = \frac{\partial^2}{\partial^2\theta} + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial^2\phi} + \frac{\partial^2}{\partial^2\psi}\right) - 2\frac{\cos\theta}{\sin^2\theta}\frac{\partial}{\partial\phi}\frac{\partial}{\partial\psi} + \cot\theta\frac{\partial}{\partial\theta}, \qquad (136)$$

$$(D_{\alpha})^2_3 = \frac{\partial^2}{\partial^2\psi}.$$

$\Delta_q$ is the Laplace operator in Cartesian coordinates.

We define the new density $P(t,q,\phi,\theta)$,

$$P(t,q,\phi,\theta) = \int d\psi\, P(t,q,\phi,\theta,\psi). \qquad (137)$$

Integrating Eq. (135) on both sides with respect to $\psi$ leads to

$$\frac{\partial}{\partial t} P(t,q,\phi,\theta) = kT\left[a\Delta_q + (a_3 - a)\frac{\partial}{\partial q}\cdot B(\phi,\theta)\frac{\partial}{\partial q} + b\Delta\,|_{r=1}\right] P(t,q,\phi,\theta). \qquad (138)$$

The matrix $B(\alpha)$ defined in Eq. (136) does not depend on $\psi$.

$$B(\phi,\theta) = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\cos\phi \\ \cos\theta \end{pmatrix} \otimes \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\cos\phi \\ \cos\theta \end{pmatrix}. \qquad (139)$$

The contributions of Eq. (135) which contain a derivative with respect to $\psi$ vanish after integrating by parts. Therefore the operator $D^2_{\alpha}$ reduces to $\Delta\,|_{r=1}$, the Laplace operator in spherical coordinates on the unit sphere.

$$D^2_{\alpha}\,|_{\psi} = \Delta\,|_{r=1}. \qquad (140)$$

We assume that the initial condition factorizes. For $t > t_0$ the solution of (138) has the form

$$P(t_0,q,\phi,\theta) = P_{0t}(q)P_{0R}(\phi,\theta),$$
$$P(t,q,\phi,\theta) = P_T(t,[P_R\,])P_R(t,\phi,\theta), \qquad t > t_0. \qquad (141)$$

The function $P_T(t)$ is also a functional of the distribution $P_R(t)$. $P_T(t)$ and $P_R(t)$ are probability densities, $\int d^3q\, P(t,q,[P_R\,]) = 1$ and $\int d\phi d\theta \sin\theta P_R(t,\phi,\theta) = 1$ for all times $t > t_0$. The boundary conditions are: $P_T(t,q,[P_R\,]) = 0$ if $q_i = \infty$ for some $i = 1,2,3$. Substituting (141) into Eq. (138) and integrating with respect to $\phi$ and $\theta$ (using the weight $\sin\theta$) leads to Eq. (142). Similarly one obtains (143) by integrating with respect to $q$.

$$\frac{\partial}{\partial t} P_T(t,q,[P_R]) = kT \Big\{ a\Delta_q + (a_3 - a) \times \sum_{ij} \int d\phi \sin\theta d\theta B_{ij}(\phi,\theta) P_R(t,\phi,\theta) \frac{\partial}{\partial q_i} \frac{\partial}{\partial q_j} \Big\} \times P_T(t,q,[P_R]), \tag{142}$$

$$\frac{\partial}{\partial t} P_R(t,\phi,\theta) = kTb\Delta \Big|_{r=1} P_R(t,\phi,\theta) \quad \text{for } t \geqslant t_0. \tag{143}$$

The second equation describes the "Brownian motion on the unit sphere." The eigenfunction of $\Delta\,|_{r=1}$ are the spherical harmonics $Y_{1m}(\theta,\phi)$. Substituting a solution $P_R(t,\phi,\theta)$ of (143) into Eq. (142) one obtains an expression which is formally a diffusion equation with time-dependent diffusion coefficients. The off diagonal elements of the diffusion matrix vanish if the distribution $P_R(t,\phi,\theta)$ is uniform.

Similarly, one can show that for arbitrary molecules with $C_{TR} = 0$ a solution of the form (141) (including $\psi$) exists, if the positions and orientations are uncorrelated at time $t = t_0$ and if $U = 0$.

### B. Diffusion in two dimensions

In two dimensions the diffusion equation without external potential can be solved for arbitrary initial conditions. Equation (108) reduces to

$$\frac{\partial}{\partial t} P(t,q_1,q_2,\phi) = AP(t,q_1,q_2,\phi), \tag{144}$$

$$A = \begin{pmatrix} \frac{\partial}{\partial q_1} \\ \frac{\partial}{\partial q_2} \end{pmatrix} \cdot \Lambda(\phi) \begin{pmatrix} \frac{\partial}{\partial q_1} \\ \frac{\partial}{\partial q_2} \end{pmatrix} + kT\gamma \frac{\partial^2}{\partial^2\phi}, \quad t \geqslant t_0$$

$$\Lambda(\phi) = kT \begin{pmatrix} \alpha\cos^2\phi + \beta\sin^2\phi & (\beta-\alpha)\sin\phi\cos\phi \\ (\beta-\alpha)\sin\phi\cos\phi & \alpha\sin^2\phi + \beta\cos^2\phi \end{pmatrix}. \tag{145}$$

$kT\alpha$, $kT\beta$, and $kT\gamma$ are the diffusion constants corresponding to the degrees of freedom $q_1$, $q_2$, and $\phi$. We assume that $\alpha > \beta$. We use the following identities to simplify the matrix $\Lambda(\phi)$:

$$\alpha\cos^2\phi + \beta\sin^2\phi = \frac{\alpha+\beta}{2} + \frac{\alpha-\beta}{2}\cos 2\phi,$$
$$\alpha\sin^2\phi + \beta\cos^2\phi = \frac{\alpha+\beta}{2} - \frac{\alpha-\beta}{2}\cos 2\phi, \tag{146}$$
$$2\sin\phi\cos\phi = \sin 2\phi,$$

$$\Lambda(\phi) = kT\delta \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + kT\epsilon \begin{pmatrix} \cos 2\phi & -\sin 2\phi \\ -\sin 2\phi & -\cos 2\phi \end{pmatrix}. \tag{147}$$

$\delta$ is the average translational diffusion constant and $\epsilon$ is a measure for the asymmetry of the particle.

$$\delta \equiv \frac{\alpha+\beta}{2}, \quad \epsilon \equiv \frac{\alpha-\beta}{2}. \tag{148}$$

Without solving (144) explicitly it is already possible to make some statements about the lowest moments of $q_1$, $q_2$, and $\phi$. One obtains the following differential equations for the expectation values $\langle\cdots\rangle_t = \int dq_1\, dq_2\, d\phi \cdots P(t,q_1,q_2,\phi)$:

$$\frac{d}{dt}\langle q_1\rangle_t = 0,$$
$$\frac{d}{dt}\langle q_1^2\rangle_t = 2kT\delta + 2kT\epsilon\langle\cos 2\phi\rangle_t,$$
$$\frac{d}{dt}\langle q_1 q_2\rangle_t = -2kT\epsilon\langle\sin 2\phi\rangle_t, \tag{149}$$
$$\frac{d}{dt}\langle\cos 2\phi\rangle_t = -4\gamma kT\langle\cos 2\phi\rangle_t,$$
$$\frac{d}{dt}\langle\sin 2\phi\rangle_t = -4\gamma kT\langle\sin 2\phi\rangle_t.$$

This leads to

$$\langle\cos 2\phi\rangle_t = e^{-4\gamma kTt}\langle\cos 2\phi\rangle_{t_0},$$
$$\langle q_1^2\rangle_t = 2kT\delta t + \frac{\epsilon}{2\gamma}(1 - e^{-4\gamma kTt})\langle\cos 2\phi\rangle_{t_0} + \langle q_1^2\rangle_{t_0}, \tag{150}$$
$$\langle q_1 q_2\rangle_t = \frac{-\epsilon}{2\gamma}(1 - e^{-4\gamma kTt})\langle\sin 2\phi\rangle_{t_0} + \langle q_1 q_2\rangle_{t_0}.$$

The calculation of arbitrary expectation values $\langle 0\rangle_t$, $0 = 0(q_1,q_2,\phi)$ can be reduced to the problem of finding the eigenvectors and eigenvalues of the diffusion operator $A$ in Eq. (144).

$$(A - \lambda_{k_1k_2l})\psi_{k_1k_2l} = 0. \tag{151}$$

For the symmetric case $\alpha = \beta$ the solutions of (151) are

$$\psi'_{k_1k_2l}(q_1,q_2,\phi) = \frac{1}{\pi^{1/2}}\frac{1}{L} e^{ik_1q_1} e^{ik_2q_2} \sin(l\phi),$$
$$\psi_{k_1k_2l}(q_1,q_2,\phi) = \frac{1}{\pi^{1/2}}\frac{1}{L} e^{ik_1q_1} e^{ik_2q_2} \cos(l\phi). \tag{152}$$

We choose a box of length $L$ and assume periodic boundary conditions,

$$\psi(0,q_2,\phi) = \psi(L,q_2,\phi), \quad \psi(q_1,0,\phi) = \psi(q_1,L,\phi),$$
$$\psi(q_1,q_2,\phi) = \psi(q_1,q_2,\phi + 2\pi). \tag{153}$$

The possible values for $k_1$, $k_2$, and $l$ are

$$k_1 = \pm\frac{2n\pi}{\lambda}, \quad k_2 = \pm\frac{2m\pi}{L}, \quad n,m\in N$$
$$l = 0,1,2,\ldots. \tag{154}$$

In the general case $\alpha > \beta$ we make the ansatz that the eigenfunctions can be written

$$\psi_{k_1k_2l}(q_1,q_2,\phi) = \frac{1}{\pi^{1/2}}\frac{1}{L} e^{ik_1q_1} e^{ik_2q_2} g_{k_1k_2l}(\phi). \tag{155}$$

One obtains the following differential equation for the unknown function $g_{k_1k_2l}(\phi)$ [(144), (147), (151)]:

$$\left[ -\delta(k_1^2+k_2^2)-\epsilon(k_1^2-k_2^2)\cos 2\phi + 2\epsilon k_1 k_2 \sin 2\phi + \gamma\frac{\partial^2}{\partial\phi^2} - \frac{\lambda_{k_1k_2l}}{kT}\right] g_{k_1k_2l}(\phi) = 0. \tag{156}$$

We define the complex wavenumber $k'$,

$$k' \equiv k_1 + ik_2, \qquad \psi \equiv \arctan(k_2/k_1). \tag{157}$$

$k'$ can be written $k' = |k'|l^{i\psi}$. Equation (156) becomes

$$\left\{ -\left(\delta|k'|^2 + \frac{\epsilon}{2}|k'|^2 e^{2i\phi+2i\psi} + \frac{\epsilon}{2}|k'|^2 e^{-2i\phi-2i\psi}\right) + \gamma^2\frac{\partial^2}{\partial\phi^2} - \frac{\lambda_{k_1k_2l}}{kT}\right\} g_{k_1k_2l}(\phi) = 0. \tag{158}$$

The exponentials can be combined to $\cos(2[\phi+\psi])$. Equation (158) is equivalent to Mathieu's equation.[16]

$$\frac{d}{dz}y_l(z) + (a_l(r) - 2r\cos 2z)y_l(z) = 0, \tag{159}$$

$$r = \frac{(k_1^2+k_2^2)(\alpha-\beta)}{4\gamma},$$

$$z = \phi + \arctan(k_2/k_1), \tag{160}$$

$$\lambda_{k_1k_2l} = -kT\left\{\gamma a_l(r) + \frac{\alpha+\beta}{2}(k_1^2+k_2^2)\right\},$$

$$g_{k_1k_2l}(\phi) = y_l[\phi + \arctan(k_2/k_1)].$$

The eigenvalues $a_l(r)$ of Mathieu's equation are negative for certain values of $r$ and $l$,[16] but the eigenvalues $\lambda_{k_1k_2l}$ are always less or equal to zero for all $k_1k_2$, and $l$.

Equation (159) has a complete set of orthogonal solutions $ce_l(r,z)$ and $se_l(r,z)$ with the corresponding eigenvalues denoted by $a_l(r)$ and $b_l(r)$.[16] The eigenfunctions of (151) are

$$\psi'_{k_1k_2l}(q_1,q_2,\phi) = \frac{1}{\pi^{1/2}}\frac{1}{L}e^{ik_1q_1}e^{ik_2q_2}se_l(r,\phi+\arctan(k_2/k_1))$$

$$\psi_{k_1k_2l}(q_1,q_2,\phi) = \frac{1}{\pi^{1/2}}\frac{1}{L}e^{ik_1q_1}e^{ik_2q_2}ce_l(r,\phi+\arctan(k_2/k_1)). \tag{161}$$

since $\{\psi'_{k_1k_2l},\psi_{k_1k_2l}\}$ is a complete set of orthogonal eigenfunctions of the diffusion operator (151), the expectation value $\langle 0\rangle_t$ can be found by

$$\langle 0\rangle_t = \int dq_1\,dq_2 d\phi\, P(t,q_1,q_2,\phi)\,O(q_1,q_2,\phi) = \sum_{k_1k_2l} e^{\lambda_{k_1k_2l}t}P_{k_1k_2l}\,O_{k_1k_2l} + \sum_{k_1k_2l} e^{\lambda'_{k_1k_2l}t}P'_{k_1k_2l}\,O'_{k_1k_2l}. \tag{162}$$

The coefficients $O_{k_1k_2l}, O'_{k_1k_2l}, P_{k_1k_2l}, P'_{k_1k_2l}$ are obtained from $O(q_1,q_2,\phi)$ and the initial distribution $P(t_0,q_1,q_2,\phi)$.

$$\begin{aligned} O_{k_1k_2l} &= \int dq_1\,dq_2\,d\phi\,\psi^*_{k_1k_2l}(q_1,q_2,\phi)\,O(q_1,q_2,\phi) \equiv (\psi_{k_1k_2l},0),\\ O'_{k_1k_2l} &= (\psi'_{k_1k_2l},0),\\ P_{k_1k_2l} &= (P(t_0),\psi_{k_1k_2l}),\\ P'_{k_1k_2l} &= (P(t_0),\psi'_{k_1k_2l}). \end{aligned} \tag{163}$$

As an illustration we consider the following two observables:

$$O^s(q_1,\phi) \equiv \sin(k_1q_1)se_1(r,\phi), \qquad O^c(q_1,\phi) \equiv \sin(k_1q_1)ce_1(r,\phi), \tag{164}$$

with $k_1 = 2\pi/L$ and $r = \pi^2(\alpha-\beta)/\gamma L^2$. We assume that the asymmetry is small. In this case $r \ll 1$ and the Mathieu functions $se_1$ and $ce_1$ are approximately

$$ce_1(r,\phi) \cong \cos(\phi) - \frac{r}{8}\cos(3\phi), \qquad se_1(r,\phi) \cong \sin(\phi) - \frac{r}{8}\sin(3\phi). \tag{165}$$

The corresponding eigenvalues are

$$a_1(r) \cong 1 + r, \qquad b_1(r) \cong 1 - r. \tag{166}$$

The eigenvalues $\lambda_{\pm k_101}$ and $\lambda'_{\pm k_101}$ are

$$\lambda_{\pm k_101} \cong -kT\left(\gamma + \frac{\pi^2}{L^2}(3\alpha+\beta)\right), \qquad \lambda'_{\pm k_101} \cong -kT\left(\gamma + \frac{\pi^2}{L^2}(\alpha+3\beta)\right), \tag{167}$$

and for the expectation values of $O^s$ and $O^c$ one obtains

$$\langle O^c\rangle_t \cong ce^{-kT[\gamma+(\pi^2/L^2)(3\alpha+\beta)]t}, \qquad \langle O^s\rangle_t \cong c'e^{-kT[\gamma+(\pi^2/L^2)(\alpha+3\beta)]t}. \tag{168}$$

The constants $c$ and $c'$ can be written $c = (O^c,P(t_0))$ and $c' = (O^s,P(t_0))$.

The state $O^c$ decays faster since we assumed $\alpha > \beta$. $\alpha$ corresponds to the diffusion along the $e'_1$ axis of the molecule. In the state $O^c$ the molecule axis $e'_1$ is mainly parallel to the $e_1$ direction of the laboratory frame; in the state $O^s e'_1$ is mainly parallel to the $e_2$ axis. The average speed of the molecules in state $O^c$ is bigger in the direction $e_1$; $e_1$ is also the direction of the spatial inhomogenity. Therefore $O^C$ decays faster than $O^s$. This example is typical for the type of coupling of $q_1,q_2$, and $\phi$, which occurs in the translational and rotational diffusion if the otential $U$ vanishes and also $C_{TR} = 0$.

## VI. CONCLUDING REMARKS

We have shown that a "contraction of the description" is achieved when a Kramers–Liouville process is averaged with respect to its momenta variables. The second cumulant of an ordered time evolution cumulant expansion yields the generalized Smoluchowski equation as the contracted description. We have examined the details of the dynamical operator algera generated by the contraction procedure for translational and rotational degrees of freedom, and for as many as $N$ distinct particles.

A more thorough description of the higher order cumulants, shown to be small here, will appear in a forthcoming paper.

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