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Non-Markovian probability density functions with applications to itinerant oscillator models

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Starting from the linear Mori–Kubo generalized Langevin equation, conditional probability density functions are derived for independent dynamical variables of a general system under the action of (non-markovian) gaussian force or torque. The special techniques developed by Adelman (1976, 1977) for brownian oscillators are here extended to the general case.

As applications of the general theory, angular momentum and orientational probability density functions are computed for models of molecular rotation in fluids. The rotational dynamics of each molecule is described by an itinerant oscillator/librator. The periodicity of spatial orientation is treated in terms of wrapped distributions, and hence the planar-reorientational counterpart of the translational self van Hove function is derived. It is shown that both momentum and orientational probability density functions can exhibit widely varying time-decay properties, which are directly interpretable in terms of the structure and dynamics of the molecular fluid represented.

1. INTRODUCTION

Attempts have recently been made [1, 2] to treat translational and rotational molecular motions in a fluid in terms of a Langevin-type equation of motion with a non-markovian driving force or torque. This approach has great advantages in many fields. In spectroscopy it directly yields certain autocorrelation functions of orientation from which spectral information can be found, such as the complete far-infra-red/microwave spectrum, or the complete wing of Rayleigh scattered light in the depolarized regime [3]. Other autocorrelation functions can also be found, for example, those for the angular velocity or momentum of molecules with simple geometries rotating in a fluid. In general an autocorrelation function is defined as an integral over a probability density function, and in principle the latter contains more information than the former. It is therefore advantageous to be able to calculate probability density functions directly from observed spectra using as general a formalism as possible.

Adelman [4] generates conditional momentum and phase-space probability densities for brownian particles under the action of gaussian, but non-markovian, stochastic forces, and shows that these functions satisfy Fokker–Planck type equations. In § 2 of this paper we generalize Adelman's work in a straightforward manner to the case of any dynamical system under the action of gaussian stochastic force or torque, where this force is interpreted in the sense of Mori. The linear Mori–Kubo [5] generalized Langevin equation for vectors of independent dynamical variables of the system has a solution whose component variables are jointly conditionally distributed according to multivariate normal distributions. The elements of the variance–covariance matrices in the probability density functions are expressed in terms of the normalized autocorrelation functions of the variables concerned. Moreover we derive the general form of the Fokker–Planck-type equations satisfied by these probability density functions. In §§ 3 and 4 we present angular momentum and orientational probability densities for molecular rotation in fluids, where the corresponding autocorrelation functions are calculated from truncated Mori expansions, and the underlying physical model describing the rotational dynamics of each molecule is an itinerant oscillator. The orientational probability densities are wrapped normal distributions which are approximated by von Mises distributions.

Conceptual difficulties of classical brownian motion theory, and the desirability of a non-markovian approach have been emphasized by one of us elsewhere [6]. We do not restate these arguments here but accept them as basic support for our line of approach in this paper.

2. General theory

Let $\{A_j(t)\}$, $j=1, \ldots, n$, denote a linearly independent set of real-valued (implicitly) time-dependent dynamical variables of a given mechanical system. Assume that an ensemble average $\langle . \rangle$ can be defined for the system and that the set of all possible dynamical variables is a real Hilbert space in which the inner product is defined by $(A, B) \equiv \langle AB \rangle$. The set $\{A_j(t)\}$ thus spans an n-dimensional subspace of the Hilbert space.

Each variable obeys the classical Liouville equation of motion

$$\dot{A}_j(t) = \{A_j(t), H\} \equiv i\mathscr{L} A_j(t),$$

where H is the hamiltonian of the system and $i\mathscr{L}$ the Liouville operator. The solution may be written

$$A_j(t) = \exp(i\mathscr{L}t) A_j(0),$$

where the propagator $\exp(i\mathscr{L}t)$ is an orthogonal operator. The time evolution of $A_j(t)$ is therefore a rotation in Liouville space, with

$$\langle A_j(t) A_k(t) \rangle = \langle A_j(0) A_k(0) \rangle, \quad j, k = 1, \ldots, n. \tag{1}$$

If $\mathbf{A}(t)$ denotes the $n \times 1$ column vector with elements $A_j(t)$, and $\mathbf{A}^{\mathrm{T}}(t)$ its corresponding row vector, we let $\langle \mathbf{A}(t) \mathbf{A}^{\mathrm{T}}(t) \rangle$ denote the $n \times n$ matrix with elements $\langle A_j(t) A_k(t) \rangle$. From (1) it follows that

$$\langle \mathbf{A}(t) \mathbf{A}^{\mathrm{T}}(t) \rangle = \langle \mathbf{A}(0) \mathbf{A}^{\mathrm{T}}(0) \rangle. \tag{2}$$

Mori [1] shows that $\mathbf{A}(t)$ evolves in time according to the generalized Langevin equation

$$\dot{\mathbf{A}}(t) = i\Omega_{\mathbf{A}} \mathbf{A}(t) - \int_0^t d\tau \, \phi_{\mathbf{A}}(t-\tau) \mathbf{A}(\tau) + \mathbf{F}_{\mathbf{A}}(t), \tag{3}$$

where $\Omega_{\mathbf{A}}$ is a resonance frequency operator, the matrix kernel $\phi_{\mathbf{A}}(t)$ is a memory function, and $\mathbf{F}_{\mathbf{A}}(t)$ is a generalized random force or torque propagated in a special way from $\dot{\mathbf{A}}(0)$. These quantities are easily specified in terms of the projection operators P, Q defined by

$$\begin{aligned} P\mathbf{G} &\equiv \langle \mathbf{G}\mathbf{A}^{\mathrm{T}}(0) \rangle \langle \mathbf{A}(0) \mathbf{A}^{\mathrm{T}}(0) \rangle^{-1} \mathbf{A}(0), \\ Q &\equiv 1 - P, \end{aligned}$$

where P projects an arbitrary vector $\mathbf{G}$ into the subspace spanned by $\mathbf{A}(0)$, and Q projects into the orthogonal complement of this subspace. The appropriate relations are

$$\left.\begin{aligned} i\Omega_{A} &= \langle \dot{\mathbf{A}}(0) \mathbf{A}^{\mathrm{T}}(0) \rangle \langle \mathbf{A}(0) \mathbf{A}^{\mathrm{T}}(0) \rangle^{-1}, \\ F_{\mathbf{A}}(t) &= \exp(iQ\mathscr{L}t) Q \dot{\mathbf{A}}(0), \\ \phi_{\mathbf{A}}(t) &= \langle \mathbf{F}_{\mathbf{A}}(t) \mathbf{F}_{\mathbf{A}}{}^{\mathrm{T}}(0) \rangle \langle \mathbf{A}(0) \mathbf{A}^{\mathrm{T}}(0) \rangle^{-1}. \end{aligned}\right\} \tag{4}$$

The meaning of the generalized force $\mathbf{F}_{\mathbf{A}}(t)$ should not be confused with that of generalized force in classical lagrangian dynamics. In the Mori formalism of equations (3) and (4), $\mathbf{F}_{\mathbf{A}}(0)$ is the component of $\dot{\mathbf{A}}(0)$ orthogonal to $\mathbf{A}(0)$, whereas $\mathbf{F}_{\mathbf{A}}(t)$ is propagated from $\mathbf{F}_{\mathbf{A}}(0)$ by the special propagator $\exp(iQ\mathscr{L}t)$. It is easily shown that

$$\langle \mathbf{F}_{\mathbf{A}}(t) \mathbf{A}^{\mathrm{T}}(0) \rangle = 0. \tag{5}$$

The simplest physical realizations of equation (3) occur, for example, in the rotational brownian motion of a spherical top, or a disk about a fixed axis through its centre perpendicular to its plane. Equation (3) then becomes

$$\frac{D\mathbf{J}}{Dt} + \int_0^t d\tau \, \phi_{\mathbf{J}}(t-\tau) \mathbf{J}(\tau) = \mathbf{F}_{\mathbf{J}}(t), \tag{6}$$

where $\mathbf{A} = \mathbf{J}$ is the angular momentum of the rotator, the operator $\Omega_{\mathbf{J}}$ is null, $\phi_{\mathbf{J}}(t)$ is a time-dependent friction tensor, and $\mathbf{F}_{\mathbf{J}}(t)$ is a random driving torque of finite correlation time with mean $\langle \mathbf{F}_{\mathbf{J}}(t) \rangle = \mathbf{0}$. The components of each vector in (6) are referred to principal body-axes, and D/Dt denotes rate of change relative to these axes, so that $DJ_k/Dt = \dot{J}_k$. In the case of the disk there is only one component, referred to the fixed axis. For more complicated geometries non-linear terms appear in (6). Although we shall restrict ourselves in this paper to simple geometries, it is important to realize that the linear equation

$$\dot{\mathbf{J}}(t) - i\Omega_{\mathbf{J}} \mathbf{J}(t) + \int_0^t d\tau \, \phi_{\mathbf{J}}(t-\tau) \mathbf{J}(\tau) = \mathbf{F}_{\mathbf{J}}(t)$$

is formally valid for general systems, but the quantities $\Omega_{\mathbf{J}}$, $\phi_{\mathbf{J}}$ and $\mathbf{F}_{\mathbf{J}}$ defined in (4) may not have obvious physical meaning.

Reverting to general $\mathbf{A}$, equation (3) can be solved using elementary Laplace transforms, giving

$$\mathbf{A}(t) = C_{\mathbf{A}}(t) \mathbf{A}(0) + \int_0^t d\tau \, C_{\mathbf{A}}(t-\tau) \mathbf{F}_{\mathbf{A}}(\tau), \tag{7}$$

where $C_{\mathbf{A}}(t)$ is a matrix of normalized autocorrelation functions given by

$$C_{\mathbf{A}}(t) = \mathscr{L}^{-1}\{[s - i\Omega_{\mathbf{A}} + \hat{\phi}_{\mathbf{A}}(s)]^{-1}\} = \langle \mathbf{A}(t) \mathbf{A}^{\mathrm{T}}(0) \rangle \langle \mathbf{A}(0) \mathbf{A}^{\mathrm{T}}(0) \rangle^{-1}. \tag{8}$$

[Here $\hat{\phi}_{\mathbf{A}}(s)$ denotes the Laplace transform of $\phi_{\mathbf{A}}(t)$ and $\mathscr{L}^{-1}$ denotes inverse Laplace transformation. The second expression for $C_{\mathbf{A}}(t)$ in (8) follows from (7) using (5)].

If the vector $\mathbf{F}_{\mathbf{A}}(t)$ is a multivariate gaussian process with mean $\langle \mathbf{F}_{\mathbf{A}}(t)\rangle$, and if the initial vector $\mathbf{A}(0)$ at time $t=0$ is given, then it follows from (7) that $\mathbf{A}(t)$ at time $t>0$ is also a multivariate gaussian process with mean

$$\langle \mathbf{A}(t)\rangle = C_{\mathbf{A}}(t)\mathbf{A}(0) + \int_0^t d\tau\, C_{\mathbf{A}}(t-\tau)\langle \mathbf{F}_{\mathbf{A}}(\tau)\rangle.$$

In what follows we restrict ourselves to the special case $\langle \mathbf{F}_{\mathbf{A}}(t)\rangle = \mathbf{0}$ which admits the treatment of simple rotational brownian motion and simplifies the algebra generally. Then $\mathbf{A}(t)$ is conditionally distributed with the probability density function

$$p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0)) = (2\pi)^{-(1/2)n}(\det V(t))^{-1/2}$$
$$\times \exp\left[-\tfrac{1}{2}(\mathbf{A}(t)-C_{\mathbf{A}}(t)\mathbf{A}(0))^{\mathrm{T}}\, V^{-1}(t)(\mathbf{A}(t)-C_{\mathbf{A}}(t)\mathbf{A}(0))\right], \tag{9}$$

with variance–covariance matrix

$$\begin{aligned} V(t) &= \langle(\mathbf{A}(t)-C_{\mathbf{A}}(t)\mathbf{A}(0))(\mathbf{A}(t)-C_{\mathbf{A}}(t)\mathbf{A}(0))^{\mathrm{T}}\rangle \\ &= \langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle - C_{\mathbf{A}}(t)\langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle C_{\mathbf{A}}{}^{\mathrm{T}}(t). \end{aligned} \tag{10}$$

We see from (10) that the elements of $V(t)$ may be calculated directly from the elements of the normalized autocorrelation matrix $C_{\mathbf{A}}(t)$, so that if the elements of $C_{\mathbf{A}}(t)$ can be found, experimentally or otherwise, then the conditional probability density function $p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0))$ can be calculated directly from (9).

It is clearly of fundamental importance to know whether or not the generalized force $\mathbf{F}_{\mathbf{A}}(t)$ is a gaussian process. This depends both on the nature of $\mathbf{A}(t)$ and on the geometry. For example, if we consider the angular velocity $\boldsymbol{\omega}$ of the sphere or disk mentioned above, the corresponding random driving torque $\mathbf{F}_{\omega}(t)$ may be assumed gaussian (although non-markovian), and so $\boldsymbol{\omega}$ is conditionally gaussian. If however we consider the total Euler angle

$$\theta(t) = \int_0^t \omega_1(\tau)\, d\tau,$$

then $F_{\theta}(t)$ is not gaussian, so that $p(\theta(t)\,;\ t|\theta(0))$ does not have the form of (9) [7]. [See equation (25), however, for $p(\theta(t)\,;\ t|\theta(0), \dot{\theta}(0))$.] Here $\boldsymbol{\theta}$ is total angle turned through in time t, rather than the angular orientation which is restricted to the range $-\pi \leqslant \theta \leqslant \pi$. The angular orientation has a wrapped normal distribution which we shall consider in § 4. In general the gaussian or non-gaussian nature of $\mathbf{F}_{\mathbf{A}}(t)$ for a given $\mathbf{A}(t)$ can be investigated by expanding the operator $\exp(iQ\mathscr{L}t)$ in (4). Since Q and $\mathscr{L}$ commute, and $Q^n = Q$ for $n \geqslant 1$, we have

$$\mathbf{F}_{\mathbf{A}}(t) = Q\dot{\mathbf{A}}(0) + tQi\mathscr{L}\dot{\mathbf{A}}(0) - \tfrac{1}{2}t^2\, Q\mathscr{L}^2\, \dot{\mathbf{A}}(0) + \dots .$$

As a simple illustration we may consider $F_{\theta}(t)$ for the disk rotating in its plane under a gaussian restoring torque $\Gamma(t) = -\tau[\theta(t)-\theta(0)]$. The Liouville operator is $i\mathscr{L} = I\dot{\theta}(\partial/\partial\theta) - \tau\theta(\partial/\partial\dot{\theta})$, where I is the moment of inertia of the disk, so that $(i\mathscr{L})^{2m}\dot{\theta} = (-I\tau)^m\dot{\theta}$ and $(i\mathscr{L})^{2m+1}\dot{\theta} = I^m(-\tau)^{m+1}\theta$. Since $Q\theta(0) = 0$ and $Q\dot{\theta}(0) = \dot{\theta}(0)$ it follows that

$$\begin{aligned} F_{\theta}(t) &= \dot{\theta}(0)\left[1 - \frac{1}{2!}\, I\tau t^2 + \frac{1}{4!}\,(I\tau)^2\, t^4 - \dots\right] \\ &= \dot{\theta}(0)\cos[(I\tau)^{1/2}t]. \end{aligned}$$

Similarly we can show that $F_{\dot{\theta}}(t) = (\Gamma(0)/I)\cos((I\tau)^{1/2}t)$, so that $F_{\dot{\theta}}(t)$ is gaussian, while $F_{\theta}(t)$ is not.

To complete the generalization of Adelman's work we show that the probability density function defined in (9) satisfies the generalized Fokker–Planck equation

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial \mathbf{A}}\cdot(\dot{C}_{\mathbf{A}}C_{\mathbf{A}}{}^{-1}\,\mathbf{A}p) + \tfrac{1}{2}\frac{\partial}{\partial \mathbf{A}}\cdot\left[C_{\mathbf{A}}\frac{d}{dt}(M^{-1})C_{\mathbf{A}}{}^{\mathrm{T}}\frac{\partial p}{\partial \mathbf{A}}\right], \tag{11}$$

where $\mathbf{A} \equiv \mathbf{A}(t)$, $C_{\mathbf{A}} \equiv C_{\mathbf{A}}(t)$, and $M = C_{\mathbf{A}}{}^{\mathrm{T}}\, V^{-1}\, C_{\mathbf{A}}$. Equation (11) is exact for non-markovian, gaussian systems and is similar in structure to the Fokker–Planck equations derived in markovian theory from the classical Schmolukowski–Chapman–Kolmogorov [8] relation. This last relation is not valid in the non-markovian regime, and we must derive (11) by direct means. The main steps of the derivation are given in the Appendix. Particular forms of (11) emerge [4] when the elements of $\mathbf{A}$ are uncorrelated, and also for phase-space variables of the form $\mathbf{A} = \begin{pmatrix}\mathbf{a}\\ \dot{\mathbf{a}}\end{pmatrix}$, but we shall not be concerned with such probability density functions in this paper.

In our treatment of orientation in § 4 we will need probability densities of the form $p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0), \dot{\mathbf{A}}(0))$ rather than $p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0))$. We will require certain cross-correlations between $\mathbf{A}$ and $\dot{\mathbf{A}}$. Writing $\dot{\mathbf{A}}$ for $\mathbf{A}$ in (3) we obtain

$$\ddot{\mathbf{A}}(t) = i\Omega_{\dot{\mathbf{A}}}\dot{\mathbf{A}}(t) - \int_0^t d\tau\, \phi_{\dot{\mathbf{A}}}(t-\tau)\dot{\mathbf{A}}(\tau) + \mathbf{F}_{\dot{\mathbf{A}}}(t), \tag{12}$$

which may be solved as in (7) to give

$$\mathbf{A}(t) = \mathbf{A}(0) + X_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0) + \int_0^t d\tau\, X_{\dot{\mathbf{A}}}(t-\tau)F_{\dot{\mathbf{A}}}(\tau), \tag{13}$$

where $X_{\dot{\mathbf{A}}}(t)$ is a cross-correlation matrix given by

$$X_{\dot{\mathbf{A}}}(t) = \mathscr{L}^{-1}\{[s^2 - i\Omega_{\dot{\mathbf{A}}} + s\hat{\phi}_{\dot{\mathbf{A}}}(s)]^{-1}\} = \langle \mathbf{A}(t)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle\, \langle \dot{\mathbf{A}}(0)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle^{-1}. \tag{14}$$

We may also write

$$\dot{X}_{\dot{\mathbf{A}}}(t) = \langle \dot{\mathbf{A}}(t)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle\, \langle \dot{\mathbf{A}}(0)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle^{-1} = C_{\dot{\mathbf{A}}}(t),$$

so that

$$X_{\dot{\mathbf{A}}}(t) = \int_0^t C_{\dot{\mathbf{A}}}(\tau)\, d\tau + X_{\dot{\mathbf{A}}}(0). \tag{15}$$

$X_{\dot{\mathbf{A}}}(t)$ is also related to $C_{\mathbf{A}}(t)$ by

$$X_{\dot{\mathbf{A}}}(t) = -\dot{C}_{\mathbf{A}}(t)\langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle\, \langle \dot{\mathbf{A}}(0)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle^{-1},$$

so that

$$C_{\mathbf{A}}(t) = 1 - \int_0^t d\tau\, X_{\dot{\mathbf{A}}}(\tau)\langle \dot{\mathbf{A}}(0)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle\, \langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle^{-1} \tag{16}$$

and

$$C_{\dot{\mathbf{A}}}(t) = -\ddot{C}_{\mathbf{A}}(t)\langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle\, \langle \dot{\mathbf{A}}(0)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle^{-1}. \tag{17}$$

The conditional probability density function

$$p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0), \dot{\mathbf{A}}(0)) = (2\pi)^{-(1/2)n}(\det W(t))^{-1/2}$$
$$\times \exp\left[-\tfrac{1}{2}(\mathbf{A}(t)-\mathbf{A}(0)-X_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))W^{-1}(t)(\mathbf{A}(t)-\mathbf{A}(0)-X_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))^{\mathrm{T}}\right] \tag{18}$$

is inferred from (13) when $\langle \mathbf{F}_{\dot{\mathbf{A}}}(t)\rangle = \mathbf{0}$, with variance–covariance matrix

$$\begin{aligned} W(t) &= \langle(\mathbf{A}(t)-\mathbf{A}(0)-X_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))(\mathbf{A}(t)-\mathbf{A}(0)-X_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))^{\mathrm{T}}\rangle \\ &= 2(1-C_{\mathbf{A}}(t))\langle\mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle - X_{\dot{\mathbf{A}}}(t)\langle\dot{\mathbf{A}}(0)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle X_{\dot{\mathbf{A}}}{}^{\mathrm{T}}(t) \\ &= 2\int_0^t d\tau\, X_{\dot{\mathbf{A}}}(\tau)\langle\dot{\mathbf{A}}(0)\dot{\mathbf{A}}(0)\rangle - X_{\dot{\mathbf{A}}}(t)\langle\dot{\mathbf{A}}(0)\dot{\mathbf{A}}^{\mathrm{T}}(0)\rangle X_{\dot{\mathbf{A}}}{}^{\mathrm{T}}(t). \end{aligned} \tag{19}$$

Thus $p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0),\ \dot{\mathbf{A}}(0))$ is readily calculated from (15), (18) and (19) from a knowledge of $C_{\dot{\mathbf{A}}}(t)$. We note that this probability density also satisfies a generalized Fokker–Planck equation analogous to (11).

3. Angular momentum probability density functions

Consider the angular momentum J of the disk rotating in its plane. If I is its moment of inertia about the axis of rotation, k is Boltzmann's constant, and T the temperature, then $\langle J^2(0)\rangle = kTI$, and the normalized angular momentum autocorrelation function is

$$C_J(t) = \frac{\langle J(t)J(0)\rangle}{kTI}.$$

The corresponding probability density function is

$$p(J\,;\ t|J(0)) = [2\pi kTI(1-C_J{}^2(t))]^{-1/2} \exp\left[-\frac{(J-C_J(t)J(0))^2}{2kTI(1-C_J{}^2(t))}\right], \tag{20}$$

which satisfies the Fokker–Planck equation

$$\frac{\partial p}{\partial t} = \beta(t)\left[\frac{\partial}{\partial J}(Jp) + kTI\frac{\partial^2 p}{\partial J^2}\right], \tag{21}$$

with $\beta(t) = -\dot{C}_J(t)/C_J(t)$, and initial condition $p(J\,;\ 0|J(0)) = \delta(J-J(0))$.

In this paper we inject various forms of $C_J(t)$ for disk-like rotators into expression (20) and compute $p(J\,;\ t|J(0))$ at various times. [The same results were obtained by injecting $\beta(t)$ into (21) and solving the resulting partial differential equation numerically.] The analytical expression we have used for $C_J(t)$ is

$$C_J(t) = \left[\frac{\cos\beta t}{1+\Gamma} + \frac{1}{\beta}\left(\frac{\alpha_1+\Gamma\alpha_2}{1+\Gamma}\right)\sin\beta t\right]\exp(-\alpha_1 t) + \frac{\Gamma}{1+\Gamma}\exp(-\alpha_2 t), \tag{22}$$

where α_1, α_2, β and Γ are constants (defined later). Its derivation [6] is based on a truncated Mori expansion equivalent to a three-variable Kivelson–Keyes theory [9]. Coffey and Calderwood [10] have shown recently that this type of $C(t)$ agrees with that obtained from the itinerant oscillator model for resonance (Poley) absorption in dipolar liquids after accounting for inertial effects.

The physical significance of our disk-like model can thus be clarified. A librating central molecule is represented by a disk, and its cage of neighbours by an annulus, large in comparison with the disk. The disk and annulus are coplanar and concentric and are free to rotate about the same central axis perpendicular to their plane. The disk carries a dipole $\boldsymbol{\mu}$ along a diameter whose spatial orientation, $\theta(t)$, is measured relative to the fixed direction of an applied alternating field. The spatial orientation, $\psi(t)$, of the annulus is also measured relative to this fixed direction. The following properties are then assumed :

(i) the dipole is attracted towards the direction in space specified by $\psi(t)$ under a restoring torque proportional to the angular displacement $\theta(t)-\psi(t)$;

(ii) the electrical interaction between neighbouring molecules is negligible and an average cage containing a molecule behaves in the same way ;

(iii) a steady electric field applied for a long time has preferentially oriented the dipole axes on average towards its own direction, and then the field is suddenly removed ;

(iv) the damping and random torques arising from the surroundings of a system act only on the annulus, while the resulting motion of the disk is described by (6).

If I_1 and I_2 are the moments of inertia of annulus and disk, respectively, about the central axis, ω_0 is the angular frequency of the disk when the annulus is held stationary, and γ is a coefficient defined by $kT\tau_{\mathrm{D}}/I_1$, where τ_{D} is the Debye relaxation time, then the Laplace transform of $C_J(t)$ is

$$\hat{C}_J(s) \propto \frac{s^2+s\gamma+K_1(0)}{s^3+s^2\,\gamma+s(K_0(0)+K_1(0))+\gamma K_0(0)}, \tag{23}$$

where

$$K_0(0) = \omega_0{}^2, \quad K_1(0) = (I_2/I_1)K_0(0). \tag{24}$$

Writing the zeros of the denominator in (23) as $-\alpha_2$, $-\alpha_1 \pm i\beta$, the inverse transform is given by (22), where

$$\Gamma = \frac{2\alpha_1(2\beta^2-\alpha_1{}^2)}{\alpha_2(3\alpha_1{}^2-\beta^2-\alpha_2{}^2)}.$$

Equations (24) show that in this model the libration peak frequency of the far-infra-red (ω_0) is proportional to the root mean square torque, so that the higher the torque the higher is the peak frequency of the Poley absorption. In every instance considered in this paper we have $K_1(0) > K_0(0)$ so that $I_2 > I_1$, i.e. we are always considering the motion of a heavy disk inside a light annulus. In chemical terms we are approximating the angular dynamics of a massive, dipolar, disk-like solute (or alternatively an asymmetric top whose dipole rotates in a plane) in a dilute solution of much lighter (preferably non-dipolar) solvent molecules, so that induced absorption neglected by condition (ii) above is minimized.

In the limit of rotational diffusion, which implies infinitesimally small changes of angular momentum taking place infinitely fast, the derivative $\dot{J}$ is singular at certain points in the time domain and ω_0 shifts towards infinity, so that the Poley peak is replaced by a plateau in the optical absorption coefficient. On the other hand, for a collision-free gas, $C_J(t)$ remains at its initial value and $K_0(0)$ as well as $K_1(0)$ vanish. In this limit equation (23) is unphysical since $\hat{C}_J(s) \to 1/s$ and the theoretical $C_J(t)$ is not time-dependent.

In the region where $I_2 \gtrsim I_1$ and ω_0 is small, $C_J(t)$ decays with an initial Kummer-like dependence, becoming exponential thereafter. As the torque derivative term $K_1(0)$ becomes increasingly large with respect to $K_0(0)$ (I_2 becoming large with respect to I_1), then $C_J(t)$ looks more like a pure exponential, except at the origin which is always approached with zero slope for the classical autocorrelation function. Clearly the angular dynamics corresponding to $K_1(0) \gtrsim K_0(0)$ and $K_1(0) \gg K_0(0)$ must be very different although the angular momentum autocorrelation function itself varies very little in its time decay characteristics. Furthermore, it is virtually indistinguishable from the ex-potential and the underlying dynamical process might be mistaken quite easily for something simpler than reality. In general $C_J(t)$ is a complicated damped-oscillatory function of time both in our analytic expression [11] and from the results of computer simulations [10] in ensembles of $\sim 10^2$ potentials.

In contrast our calculated probability density functions exhibit widely different decays for each $K_1(0)$, $K_0(0)$ pair, and are directly interpretable in terms

Parameters used to calculate $C_J(t)$ of equation (22).

Figures	T/K	$\gamma/(2kT/I)^{1/2}$	$K_0(0)/(2kT/I)$	$K_1(0)/(2kT/I)$	$(2kT/I)^{1/2} \times 10^{-12}$/rad s^{-1}
1, 3	296	4·0	1·0	8·0	2·25
2, 4	340	2·0	0·78	200·0	1·44

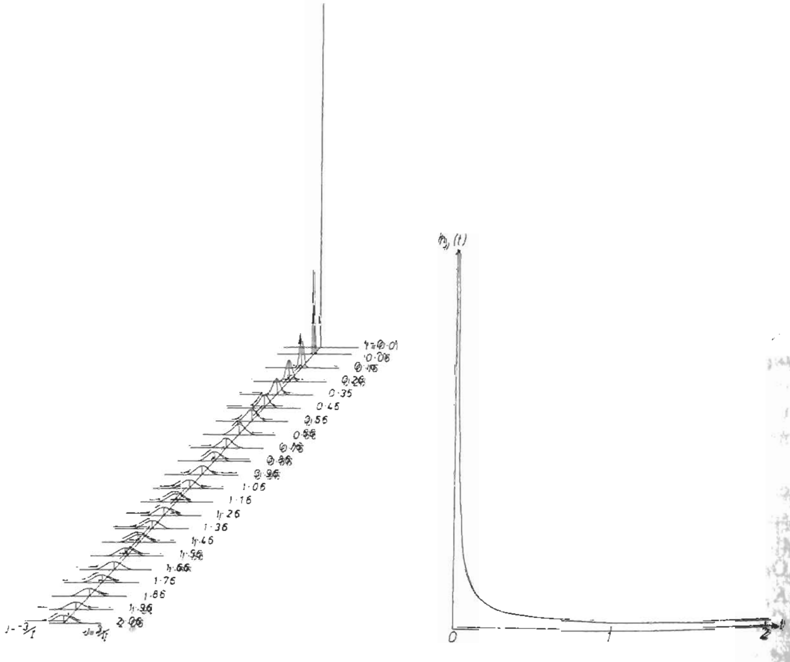

Figure 1. (*a*) $p(J;\ t|J(0))$ for $\gamma=4$, $K_0(0)=1$, $K_1(0)=8$ in reduced units (see table). p is plotted on the vertical axes, J on the horizontal axes (from $-3/I$ to $+3/I$), and time t on the diagonal axis (increasing from right to left from 0·01 ps to 2·06 ps). (*b*) Plot of p.d.f. peak-height versus time (ps).

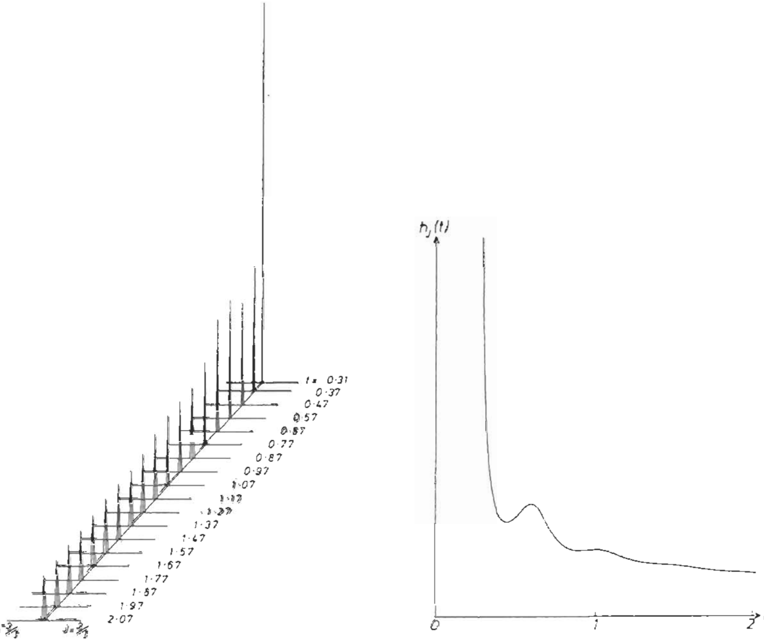

Figure 2. As for figure 1, $\gamma=2$, $K_0(0)=0{\cdot}78$, $K_1(0)=200$. Time in (*a*) from 0·31 ps to 2·07 ps.

of the structure and dynamics of the molecular fluid they represent. We consider two cases in order of increasing ratio $K_1(0)/K_0(0)$, and the parameters used to calculate $C_J(t)$ are given in the table. In each case we adopt the normalization $(2kT/I)=1$, and take $J(0)=0$. In figures 1 (*a*) and 2 (*a*) the probability densities are displayed at various times ranging from near the origin to ~ 2 ps, whereas in figures 1 (*b*) and 2 (*b*) the decay of peak-height is shown as a function of time. The curve in figure 1 (*b*) exhibits no oscillatory behaviour, decaying smoothly, although not according to the model of rotational diffusion. The torque is not subject to abrupt changes on average, i.e. the torque derivative is not large compared to the torque itself. From figure 1 (*a*) it may be inferred that the fluid as a whole is not one where the angular momentum for individual molecules is restricted to favoured values for any significant period of time, since $p(J;\ t|J(0))$ broadens out rapidly to the equilibrium distribution. Thus the fluid may be described pictorially as one where the solute molecules have a great deal of angular freedom and where collisions take place with a low mean transfer of momentum. The probability density function associated with a ratio $K_1(0)/K_0(0) \gg 1$ reveals over the same time period of ~ 2 ps quite different underlying molecular dynamics (figure 2), because the sharp peaks decay with time in an oscillatory fashion. In this case the disk is very heavy ($K_1(0)/K_0(0) = O(10^2)$) and the torque derivative is large compared with the torque itself. This means abrupt changes in the root mean square torque, which by condition (iv) above acts on the annulus. As time progresses, the oscillations in p imply that periodically it becomes increasingly probable to find a mean angular momentum which corresponds physically to a torsional motion at the bottom of an energetically favourable potential well. Here a molecule is encaged along a well-defined axis for a relatively long time, since at each successive peak maximum in p the distribution width is narrow. Hard energetic collisions are needed to affect the motion of the heavy disk.

4. Orientational probability density functions

In this section we use the angular momentum autocorrelation function $C_J(t)$ to calculate the orientational probability density function $p(\theta(t)\,;\,t|\theta(0),\dot\theta(0))$ which describes the torsional oscillation (or libration) of the dipole in an itinerant oscillator. If $\theta(t)$ is the total angle turned through in time t, then from § 2 we have

$$p(\theta(t)\,;\,t|\theta(0),\dot\theta(0))=\left[(2\pi kT/I)\left(2\int_0^t X_J(\tau)\,d\tau-X_J^2(t)\right)\right]^{-1/2}$$
$$\times\exp\left[-\frac{(\theta(t)-\theta(0)-X_J(t)\dot\theta(0))^2}{(2kT/I)(2\int_0^t X_J(\tau)\,d\tau-X_J^2(t))}\right],\qquad(25)$$

where

$$X_J(t)=\int_0^t C_J(\tau)\,d\tau,\quad\text{and here } I=I_2.$$

In practice, however, we wish $\theta(t)$ to represent the angular orientation at time t. The restricted probability density function for θ in the range $(-\pi,\pi)$ is that of a wrapped normal distribution [12] which we approximate [13] by the von Mises distribution

$$p(\theta(t)\,;\,t|\theta(0),\dot\theta(0))\approx[2\pi I_0(\alpha(t))]^{-1}$$
$$\times\exp\,[\alpha(t)\cos(\theta(t)-\theta(0)-X_J(t)\dot\theta(0))].\qquad(26)$$

The function $\alpha(t)$ can be found at any specific time t by numerically solving the equation

$$\frac{I_1(\alpha(t))}{I_0(\alpha(t))}=\exp\left[-(kT/I)\left(\int_0^t X_J(\tau)\,d\tau-\tfrac{1}{2}X_J^2(t)\right)\right],\qquad(27)$$

using standard numerical methods. I_0 and I_1 in equations (26), (27) are the modified Bessel functions of zeroth and first order, respectively.

The probability density function in (26) may be used to describe the planar libration of a dipole embedded in the inertial asymmetric top [14], since the physical picture is the same as that of the two-dimensional itinerant oscillator [15]. Recently [16] the model has been extensively tested against experimental data from Rayleigh scattering of depolarized light, far-infra-red absorptions in suitably dilute solutions of highly dipolar species in non-dipolar solvents (to avoid problems of dipole–dipole coupling [17] and induced effects [18]), and against molecular dynamics computations using the atom–atom double Lennard-Jones potential of dumbell type molecules. These studies were based on the evaluation of the planar reorientational autocorrelation function [19]

$$\langle\boldsymbol{\mu}(t)\,.\,\boldsymbol{\mu}(0)\rangle=\exp\left[-\frac{kT}{I}\int_0^t(t-\tau)\langle\dot\theta(\tau)\dot\theta(0)\rangle\,d\tau\right].\qquad(28)$$

In this evaluation the parameters $K_0(0)$, $K_1(0)$ and γ were obtained by least mean squares optimization with the experimental data on $\langle\dot{\boldsymbol{\mu}}(t)\,.\,\dot{\boldsymbol{\mu}}(0)\rangle$, a function which closely resembles [16] $C_J(t)$, and one which is conveniently observable [18] at high frequencies.

In the present paper we bypass the evaluation of any autocorrelation functions other than $C_J(t)$ and proceed directly to the orientational probability density functions in (26). [We note that $\langle\boldsymbol{\mu}(t)\,.\,\boldsymbol{\mu}(0)\rangle$ can be found, if desired, from

$$\langle\boldsymbol{\mu}(t)\,.\,\boldsymbol{\mu}(0)\rangle\equiv\int_{-\pi}^{\pi}\cos(\theta-\theta(0))p(\theta\,;\,t|\theta(0),\dot\theta(0))\,d\theta$$
$$\approx\cos(X_J(t)\dot\theta(0))\exp\left[-\frac{kT}{I}\left(\int_0^t X_J(\tau)\,d\tau-\tfrac{1}{2}X_J^2(t)\right)\right],\qquad(29)$$

which has the same form as (28) when $\dot\theta(0)=0$.] The parameters of the preceding section are used to enable a direct comparison of the two probability density functions. We adopt the same normalization as before and take $\theta(0)=0$, so that $\langle\theta(t)\rangle=\theta(0)+X_J(t)\dot\theta(0)=0$.

As illustrated in figures 3 (*a*) and 4 (*a*) the functions $p(\theta\,;\,t|\theta(0),\dot\theta(0))$ are symmetric about $\theta(0)$, eventually dying down to a flat distribution as $t\to\infty$. (The similarity in shape to gaussian distributions disappears as time increases.) The equation of the decay curve of peak-height (figures 3 (*b*) and 4 (*b*)) is

$$h_\theta(t)=\frac{\exp(\alpha(t))}{2\pi I_0(\alpha(t))},$$

as opposed to

$$h_J(t)=[2\pi kTI(1-C_J^2(t))]^{-1/2}$$

for the angular momentum J. Again the ratio $K_1(0)/K_0(0)$ is a critical factor. When this ratio is low $h_\theta(t)$ decays rapidly in a 2 ps interval (figure 3 (*b*)), but as the ratio increases the $h_\theta(t)$ curves decay more slowly and the distribution of angular displacement becomes relatively narrower (figure 4).

Whereas, for angular momentum, there is an onset of oscillation in $h_J(t)$, the decay of $h_\theta(t)$ is free of them except perhaps for the most rapid torque rate of change. Roughly speaking, this is because the oscillations are integrated out in forming $X_J(t)$. Since $K_1(0)$ is always greater than $K_0(0)$ in this paper, our probability density functions are calculated for overdamped itinerant libration, the case of experimental interest [16]. The orientational probability densities show that there is never, in the two cases studied here, a periodically increased probability of finding an individual molecule in a certain coplanar configuration relative to that at $t=0$, in contrast to the case of angular momentum. In the underdamped regime [20], however, where $K_1(0)<K_1(0)$, both $h_J(t)$ and $h_\theta(t)$ will certainly decay in a highly oscillatory fashion.

In conclusion, it is relevant to ask why these probability density functions should be evaluated in addition to the usual autocorrelation functions, and what they mean on the molecular scale. The main reason for the evaluation of

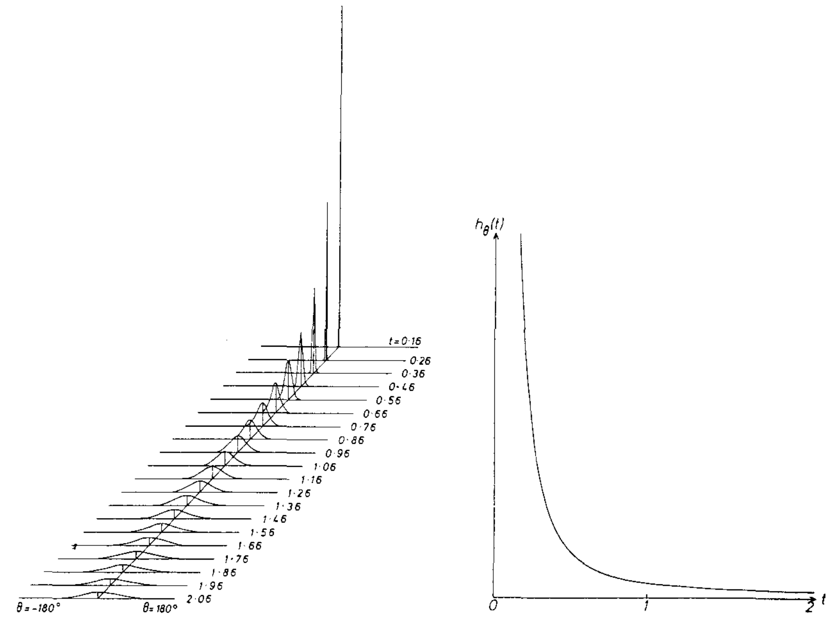

Figure 3. (*a*) $p(\theta\,;\ t\,|\,\theta(0),\ \dot\theta(0))$ for $\gamma=4$, $K_0(0)=1$, $K_1(0)=8$. θ plotted on horizontal axes (from $-180°$ to $+180°$). Time from 0·16 ps to 2·06 ps.

$p(\theta)(t)\,;\ t\,|\,\theta(0),\ \dot\theta(0))$ (apart from the obvious one mentioned in § 1 that an autocorrelation function contains less intrinsic information than the probability density function) is that it is the planar-reorientational counterpart of the translational self van Hove function [21] $G_s(\mathbf{r}\,;\ t\,|\,\mathbf{0})$. G_s may be obtained from atomic fluids by scattering thermal neutrons incoherently and inelastically. In molecular fluids, however, translation–rotation coupling is of great practical and theoretical importance, and the self-part of the observable van Hove function is in general [22] the joint probability density function $G_s(\mathbf{r},\boldsymbol{\Omega}\,;\ t\,|\,\mathbf{0},\boldsymbol{\Omega}(0))$. (For planar reorientation $\boldsymbol{\Omega}$ is replaced by the scalar θ.) Moreover, tractable expressions for the self van Hove function may be developed in the first Born approximation only if the coupling between molecular rotation and internal rotation is ignored. (The G_s function then factorizes into a product of translational and rotational counterparts.) It would be very useful, therefore, to develop the techniques in this paper into a tractable theory for the joint probability G_s, possibly within the convenient structure offered by itinerant oscillation/libration, but certainly in a form where the effect of rotation on translational diffusion (and vice versa) is considered in the laboratory frame.

Finally we should mention another class of probability density functions, namely those which satisfy generalized Fokker–Planck equations which involve the retarded kernel concept [23]. These retarded kernel equations are analytically insoluble integro-differential equations. In a forthcoming paper we shall present a numerical method for the solution of such equations and compare probability density functions thus derived with those presented here.

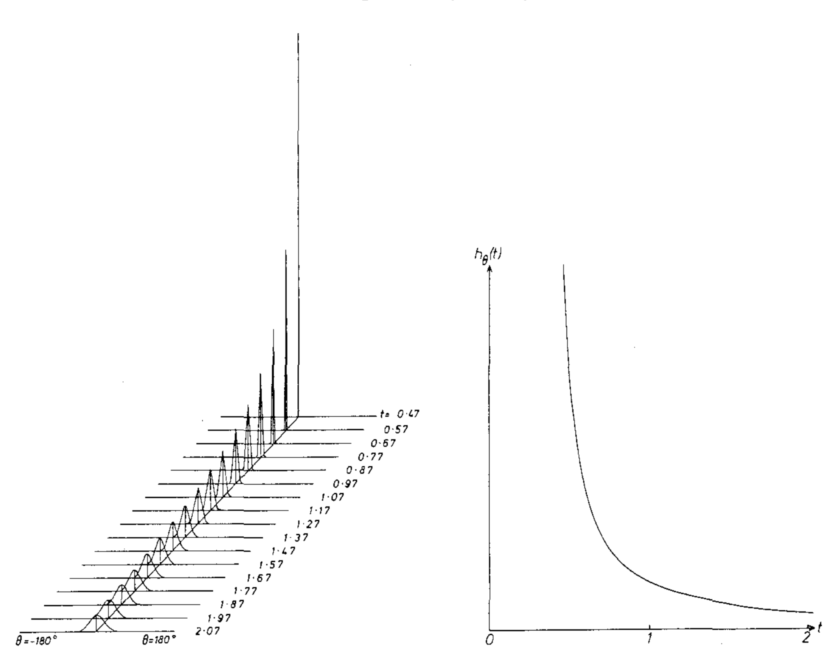

Figure 4. As for figure 3, $\gamma=2$, $K_0(0)=0{\cdot}78$, $K_1(0)=200$. Time in (*a*) from 0·47 ps to 2·07 ps.

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APPENDIX

Derivation of equation (11)

To simplify the analysis we make the change of variable $\mathbf{B}=C^{-1}\,\mathbf{A}$ ($C\equiv C_{\mathbf{A}}(t)$) and introduce the probability density function

$$q(\mathbf{B}\,;\ t\,|\,\mathbf{B}(0))\equiv p(\mathbf{A}\,;\ t\,|\,\mathbf{A}(0)).$$

Clearly $\mathbf{B}(0)=\mathbf{A}(0)$, since $C(0)=1$. Differentiating q we find

$$\frac{\partial q}{\partial t}=-\tfrac{1}{2}\left[(\det V)^{-1}\frac{d}{dt}(\det V)\right]q-\tfrac{1}{2}(\mathbf{B}-\mathbf{B}(0))\,.\,\dot M(\mathbf{B}-\mathbf{B}(0))q \qquad \text{(A 1)}$$

and

$$\frac{\partial q}{\partial \mathbf{B}}=-M(\mathbf{B}-\mathbf{B}(0))q.$$

Using the identity

$$M^{-1}\dot{M}+\frac{d}{dt}(M^{-1})M=0,$$

we have

$$\frac{\partial}{\partial \mathbf{B}}\cdot\left[\frac{d}{dt}(M^{-1})\frac{\partial q}{\partial \mathbf{B}}\right]=[\mathrm{tr}\,(M^{-1}\dot{M})-(\mathbf{B}-\mathbf{B}(0))\,.\,\dot{M}(\mathbf{B}-\mathbf{B}(0))]q.$$

From the identities

$$(\det V)^{-1}\frac{d}{dt}(\det V)=\mathrm{tr}\,(V^{-1}\dot{V})$$

and

$$\mathrm{tr}\,(V^{-1}\dot{V})+\mathrm{tr}\,(M^{-1}\dot{M})=2\,\mathrm{tr}\,(\dot{C}C^{-1}),$$

(A 1) may be rewritten in the form

$$\frac{\partial q}{\partial t}=-\mathrm{tr}\,(\dot{C}C^{-1})q+\tfrac{1}{2}\frac{\partial}{\partial \mathbf{B}}\cdot\left[\frac{d}{dt}(M^{-1})\frac{\partial q}{\partial \mathbf{B}}\right]. \qquad \text{(A 2)}$$

Returning to the original vector **A**, it is easy to show that

$$\frac{\partial q}{\partial t}=\frac{\partial p}{\partial t}+\frac{\partial p}{\partial \mathbf{A}}\dot{C}C^{-1}\mathbf{A}$$

and

$$\frac{\partial}{\partial \mathbf{B}}\cdot\left[\frac{d}{dt}(M^{-1})\frac{\partial q}{\partial \mathbf{B}}\right]=\frac{\partial}{\partial \mathbf{A}}\cdot\left[C\frac{d}{dt}(M^{-1})C^{\mathrm{T}}\frac{\partial p}{\partial \mathbf{A}}\right].$$

Substitution in (A 2) then gives (11).

Finally, we note that (11) has the associated initial condition

$$p(\mathbf{A}\,;\,0\,|\,\mathbf{A}(0))=\delta(\mathbf{A}-\mathbf{A}(0)),$$

where δ denotes the Dirac delta function.

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