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# The properties of some derivative autocorrelation functions computed with the atom–atom potential

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This note investigates autocorrelation functions (a.c.f.'s) of some derivatives of the general dynamical variable $A$ in Hilbert space, by using the method of molecular dynamics [1]. This is necessary because the equilibrium (zero-time) values of successive memory functions $K_n(t)$ in the Mori continued fraction [2] are defined [3] in terms of

$$C^{(n)}(0)=\langle A^{(n)}(0)A^{(n)}(0)\rangle,$$

where $(n)$ denotes the $n$th derivative of $A$. Thus if the $C^{(n)}(t)$ are intricate functions of time, then by implication so are the $K_n(t)[n=0, \ldots, N]$. Specifically we aim to see whether an exponential approximation [3, 4] for the memory function $K_1(t)$ is a worthwhile proposition.

A popular generalization of the Langevin equation for molecular motion in the fluid state, due originally to Kubo [5], is

$$\frac{\partial}{\partial t}\langle A(0)A(t)\rangle=i\Omega\langle A(0)A(t)\rangle-\int_0^t K(t-\tau)\langle A(0)A(\tau)\rangle\,d\tau, \tag{1}$$

where

$$i\Omega=\langle A(0)\dot{A}(0)\rangle/\langle A(0)A(0)\rangle,$$
$$=0,$$

for the classical a.c.f. from considerations of symmetry under time reversal.

The memory function $K$ can be expressed in terms of an abstract projection operator $\hat{P}$:

$$K(\tau)=\langle F(0)F(\tau)\rangle/\langle A(0)A(0)\rangle, \tag{2}$$

where

$$F(\tau)=\exp\,[i(1-\hat{P})\mathscr{L}t](1-\hat{P})i\mathscr{L}A(0),$$

and $\mathscr{L}$ is the Liouville operator. $\hat{P}$ is defined by the operation

$$\hat{P}G=[\langle AG\rangle\langle AA\rangle^{-1}]A. \tag{3}$$

The usefulness of equations (1) and (2) lies in the fact that $K$ is itself an a.c.f. (equation (2)) and obeys an equation like (1). This allowed Mori [2] to develop the set of linked Volterra equations

$$\frac{\partial}{\partial t} K_{n-1}(t) = -\int_0^t K_n(t-\tau)K_{n-1}(\tau)\,d\tau \tag{4}$$

for the set of memory functions $K_0(t) \ldots K_n(t)$. In this notation $K_{-1}(t)$ is the original a.c.f., $C(t) = \langle A(0)A(t)\rangle$. Using equation (4), analytical knowledge of the behaviour of $K_n(t)$ at times close to $t=0$ is enough, in principle, to generate the whole decay of $C(t)$ and thus its spectrum, $C(-i\omega)$. Furthermore, it can be shown [3] that the following relations are implied :

$$K_0(0) = \langle \dot{A}(0)\dot{A}(0)\rangle, \tag{5}$$

$$K_1(0) = \frac{\langle \ddot{A}(0)\ddot{A}(0)\rangle}{\langle \dot{A}(0)\dot{A}(0)\rangle} - \langle \dot{A}(0)\dot{A}(0)\rangle, \tag{6}$$

$$K_2(0) = \frac{\langle \dddot{A}(0)\dddot{A}(0)\rangle}{\langle \ddot{A}(0)\ddot{A}(0)\rangle} - \frac{[\langle \dot{A}(0)\dot{A}(0)\rangle]^3}{[\langle \dot{A}(0)\dot{A}(0)\rangle]^2}, \tag{7}$$

etc., between the memory functions and the $C^{(n)}(t)$ at the time origin. Therefore the decay with time of each member of the set $[K_0(t), K_1(t), \ldots]$ is determined by that of the successive $C^{(n)}(t)$. It is difficult and time-consuming [6] to calculate the memory functions $K_n(t)$ directly because of their definition in terms of the projection operators $\hat{P}_n$, but such is not the case for $C^{(n)}(t)$, since the predictor–corrector algorithms used in molecular dynamics to solve the Newton equations depend for their usefulness upon the calculation and storage of up to the first five derivatives of a dynamical variable $A$, typically the centre of mass velocity $\mathbf{v}$ or the total angular velocity $\boldsymbol{\omega}$ used as examples in this paper. The a.c.f.'s

$$C_1(t) = \langle \dot{\mathbf{v}}(0)\,.\,\dot{\mathbf{v}}(t)\rangle,$$

$$C_2(t) = \langle \ddot{\mathbf{v}}(0)\,.\,\ddot{\mathbf{v}}(t)\rangle,$$

$$C_3(t) = \langle \dot{\boldsymbol{\omega}}(0)\,.\,\dot{\boldsymbol{\omega}}(t)\rangle,$$

and

$$C_4(t) = \langle \ddot{\boldsymbol{\omega}}(0)\,.\,\ddot{\boldsymbol{\omega}}(t)\rangle,$$

are calculated here for a diatomic using such an algorithm due originally to Streett and Tildesley [7]. This uses the atom–atom potential [8] consisting of the Lennard-Jones atomic functions. Knowledge of $C_1(t), \ldots, C_4(t)$, and of some parent a.c.f.'s $\langle \mathbf{v}(0)\,.\,\mathbf{v}(t)\rangle$ and $\langle \boldsymbol{\omega}(0)\,.\,\boldsymbol{\omega}(t)\rangle$, calculated previously [9] using the same algorithm, makes it possible to test various truncations of the set of equations (4) suggested recently [3, 4, 10] as models for many-particle molecular dynamics. In Laplace space ($p$), equation (4) is a continued fraction :

$$\tilde{C}(p) = \frac{\tilde{C}(p)}{p + \tilde{K}_0(p)} = \frac{\tilde{C}(0)}{p + \dfrac{\tilde{K}_0(0)}{p + \tilde{K}_1(p)}} = \ldots, \tag{8}$$

and the models depend on approximating $K_0(t)$ (two-variable theory [11]) or $K_1(t)$ (three-variable theory [4, 11]) as simple functionals, most popularly single exponents. For example, Kivelson and Keyes [11] have demonstrated that the well-used $m$ and $J$-diffusion models due originally to Gordon [12] are two-variable formalisms, where $A$ is the dipole unit vector $\mathbf{u}$, defined in a linear molecule by :

$$\dot{\mathbf{u}} = \boldsymbol{\omega} \times \mathbf{u}. \tag{9}$$

These early truncations build in distinct disadvantages which manifest themselves experimentally, for example, in the far infra-red [3], where the theoretical optical absorption coefficient, $\alpha(\omega)$, regains high-frequency transparency far too slowly in comparison with observations in dipolar fluids, especially liquids. In $m$ diffusion, the power spectrum of angular velocities diverges [13] logarithmically around $\omega = 0$. It is clear from our results that $C_1(t)$ and $C_3(t)$ are oscillatory functions with negative regions, and clearly not exponential. Evans *et al.* [3, 4, 10] have demonstrated the same for $\langle \dot{\mathbf{u}}(0)\,.\,\dot{\mathbf{u}}(t)\rangle$ using spectroscopic means.

More satisfactory is an exponential $K_1(t)$ ,which is three-variable formalism with $\mathbf{u}$, for example, as the dynamical variable. This has been proposed in three or four forms [3, 4] including one by Kivelson and Madden [4] for use in dielectric studies with avoidance of the internal field problem [14]. $K_1(0)$ for angular and linear velocities is related to $C_1(0), \ldots, C_4(0)$ by equation (6). However, our results show that $C_2(t)$ and $C_4(t)$ are complicated functions of time, and by implication (equation (9)) it is unlikely that three-variable formalism can be a realistic approximation to far infra-red, microwave or depolarized Rayleigh spectra of dense molecular fluids. (This is not to say that the theory often succeeds, fortuitously, in matching the rather simple experimental curves extant from each individual technique : but less consistently the combined results [15].)

The a.c.f.'s $C_1(t), \ldots, C_4(t)$ were computed over a range of temperature ($T^*$) at constant molecular number density ($p^*$) and vice versa. In the first calculation an interatomic distance ($d^*$) of 0·3292 in reduced units [7] was used, corresponding to $N_2$. In the second we used the best available Lennard-Jones parameters for nitrogen with an interactomic distance of 0·4, so that we do not deal in this case with a ' real ' molecule. Periodic boundary conditions were used and energy and pressure were estimated with a correction for [7, 8] our assumed pair interactions. The statistical stability of the calculated a.c.f.'s was judged by using different numbers of time steps (*ca.* $5 \times 10^{-15}$ s) for the ensemble averaging. No difference could be perceived between runs of 200 and 400 steps. All the results shown here were obtained with the latter. A few runs of up to 1600 steps were carried out initially to look for any drift in quantities such as the mean-square torque and force as well as thermodynamic data. The first 100 or so steps of each run are unstable and are rejected in forming averages of any kind. This is because the molecules are fixed initially on an $\alpha$-nitrogen lattice and the initial step is complicated, involving the use of a random number generator. No a.c.f. is plotted beyond about 0·5 ps. Real time was divided into batches of up to 1200 decimal secs each of CDC 7600 (U.M.R.C.C.) time.

It is clear from figures 1 and 2 that $C_2(t)$ and $C_4(t)$ in particular are intricate functions of time, being oscillatory sometimes, sometimes very rapidly decaying, but more often with a decay on the same time scale as $C_1$ and $C_3$. Therefore were we to take the set $[\boldsymbol{\omega}, \dot{\boldsymbol{\omega}}, \ddot{\boldsymbol{\omega}}]$ or $[\mathbf{v}, \dot{\mathbf{v}}, \ddot{\mathbf{v}}]$ in a three variable formalism, the a.c.f.'s of each would decay usually on much the same time-scale, and the ' fast variable ' hypothesis [11] would be inapplicable.

The complicated analytical form of members of the set $[K_0(0), \ldots, K_n(0)]$ for $n$ greater than about 2 is clearly demonstrated in the Appendix for the orientation, dipole unit vector $\mathbf{u}$. This is so because the derivative a.c.f.'s themselves are analytically complicated functions of the mean intermolecular potential, or its derivative with respect to orientation, the root mean-square torque. The overall time dependence is supplied in great detail by a molecular dynamics calculation such as this. One of the more obvious results (figures 1 and 2) is that both $C_2$ and $C_4$ seem to be extremely sensitive to small changes in $T^*$ or $p^*$, whereas $C_1$ and $C_3$ are not at all. $C_2$ and $C_4$, being probes into the extreme short-time dynamical properties of the molecular ensemble, are revealing details about changes in the linear and angular acceleration, those changes which must be taking place during an intermolecular collision. The fact that all the a.c.f.'s exhibit negative regions is not surprising in the light that the velocity and angular velocity a.c.f.'s themselves oscillate out to fairly long times [9] at higher values of $p^*$. This is a reflection of the molecular torsional oscillation, or libration. It is not altogether surprising that $C_2$ and $C_4$ oscillate so rapidly in comparison with $C_1$ and $C_3$, the same relationship has been observed spectroscopically [4] for $\langle \mathbf{u}(0) . \mathbf{u}(t) \rangle$ and $\langle \dot{\mathbf{u}}(0) . \dot{\mathbf{u}}(t) \rangle$ ; it is merely another expression of the increased sensitivity of derivatives a.c.f.'s to short time, or high-frequency effects.

An interesting facet of the molecule motion is revealed when $C_2$ and $C_4$ are plotted together as in figures 1 and 2, since the types of decay at each different $T^*$ and $p^*$ resemble each other so closely. When one function is rapidly oscillatory, then so is the other, and the same is true when both are long-lived together. This seems to be indicative of a great deal of those translation–rotation effects, typified in the extreme case by the propellor. It is known [16] that in the Markov limit where the a.c.f. of $A$ is a single exponential, then such coupling is rigorously zero for symmetry inclusive of $C_{\infty v}$ and $D_{\infty h}$. Needless to say, the Markov limit is an unrealistic one, but under inversion $\mathbf{v} \rightarrow -\mathbf{v}$ and $\boldsymbol{\omega} \rightarrow \boldsymbol{\omega}$, whereas the Liouville operator remains unchanged. From this it follows that

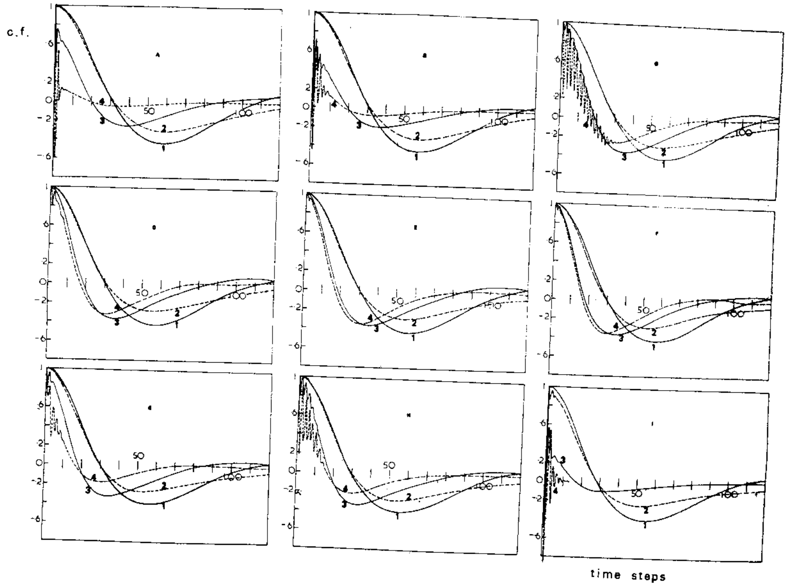

Figure 1. The autocorrelation functions $C_1(t)$ to $C_4(t)$ for constant $p^* = 0{\cdot}696$, varying $T^*$ at $d^* = 0{\cdot}3292$ ($N_2$). The a.c.f.'s above are labelled : (1) $C_1(t)$ ; (2) $C_3(t)$ ; (3) $C_2(t)$ ; (4) $C_4(t)$. (A) $T^* = 1{\cdot}50$ ; (B) $T^* = 1{\cdot}55$ ; (C) $T^* = 1{\cdot}60$ ; (D) $T^* = 1{\cdot}65$ ; (E) $T^* = 1{\cdot}70$ ; (F) $T^* = 1{\cdot}75$ ; (G) $T^* = 1{\cdot}80$ ; (H) $T^* = 1{\cdot}85$ ; (I) $T^* = 2{\cdot}00$.

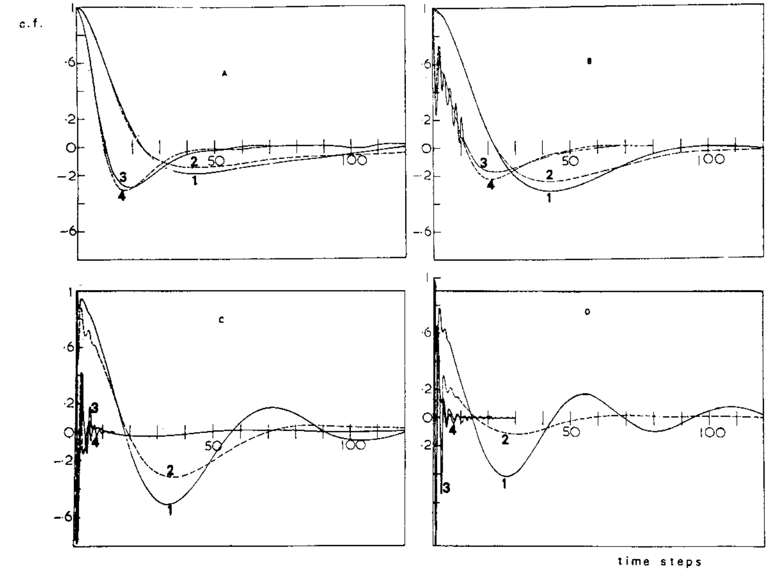

Figure 2. As for figure 1 with constant $T^* = 3{\cdot}6$, $d^* = 0{\cdot}4$. (A) $p^* = 0{\cdot}4$, (B) $p^* = 0{\cdot}6$, (C) $p^* = 0{\cdot}8$, (D) $p^* = 0{\cdot}9$.

$$C_{v\omega}(t) = -C_{v\omega}(t)$$

and so

$$\langle \mathbf{v}(0) . \boldsymbol{\omega}(t) \rangle = 0.$$

It needs to be emphasized that a similar decay rate for the velocity and angular velocity a.c.f.'s is not in itself indicative of coupling, since in the absence of any intermolecular interaction. both normalized a.c.f.'s would remain indefinitely at unity.

It remains to emphasize that the intricate nature of some of these a.c.f.'s does not imply that the memory function expansion of Mori is unusable, but the protagonists of two and three variable formalisms should note in particular the longevity of the a.c.f.'s of the higher derivatives.

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## APPENDIX

One of the ways of demonstrating the rapidly increasing complexity of the set $[K_0(0), \ldots, K_n(0)]$ with increasing $n$ is to evaluate the Maclaurin expansion and coefficients of the orientational a.c.f. $\langle \mathbf{u}(0) \,.\, \mathbf{u}(t)\rangle$, and use equations such as (4) and (5) to link these coefficients to the equilibrium averages of $K_N$. Here we carry this out for the coefficients up to that of $t^8$ in a symmetric top or linear model. The terms to be evaluated are :

$$m_0 \equiv 1 \text{ (the coefficient of } t^0),$$

$$m_2 = \langle \dot{\mathbf{u}}^2(0)\rangle, \; m_4 = \langle \ddot{\mathbf{u}}^2(0)\rangle,$$

$$m_6 = \langle \dddot{\mathbf{u}}^2(0)\rangle \text{ and } m_8 = \langle \ddddot{\mathbf{u}}^2(0)\rangle.$$

The method employed as an extension of that of Desplanques [17] which aims at an expansion of each coefficient in terms of $\boldsymbol{\omega}_\perp$, the component of the angular velocity perpendicular to the $C_{3v}$ axis. This is useful since its time derivative is a torque component, itself a derivative of a potential with respect to orientation.

Gordon [12] has evaluated $m_2$ and $m_4$ for a linear molecule, and Desplanques has extended this to the symmetric top symmetry. We have :

$$m_2 = \langle \dot{\mathbf{u}}(0) \,.\, \dot{\mathbf{u}}(0)\rangle = 2kT/I_\mathrm{B}, \tag{A}$$

$$m_4 = \langle \ddot{\mathbf{u}}(0) \,.\, \ddot{\mathbf{u}}(0)\rangle = 2\left(\frac{2kT}{I_\mathrm{B}}\right)^2\left(1+\frac{I_\mathrm{A}}{4I_\mathrm{B}}\right)+\frac{\langle T_\perp{}^2\rangle}{I_\mathrm{B}{}^2}, \tag{B}$$

where $I_\mathrm{B}$ and $I_\mathrm{A}$ are the usual moments of inertia of a symmetric top and $\langle T_\perp{}^2\rangle$ is the mean-square torque in a direction perpendicular to the $C_{3v}$ axis. Thus $K_1(0)$ is proportional to $\langle T_\perp{}^2\rangle$. The expansion of $m_6$ and $m_8$ may be accomplished by repeated differentiation of the relation

$$\dot{\boldsymbol{\omega}}_\perp = \dot{\mathbf{u}} \times \ddot{\mathbf{u}} + \mathbf{u} \times \dddot{\mathbf{u}}, \tag{C}$$

so that

$$\begin{aligned} m_6 &= \langle \dddot{\mathbf{u}}(0) \,.\, \dddot{\mathbf{u}}(0)\rangle \\ &= \langle \boldsymbol{\omega}_\perp{}^6\rangle + \langle \omega_\perp{}^2(\dot{\boldsymbol{\omega}}_\perp)^2\rangle + \langle (\ddot{\boldsymbol{\omega}}_\perp)^2\rangle \\ &\quad + \tfrac{5}{2}\left\langle \left[\frac{d}{dt}(\omega_\perp{}^2)\right]^2\right\rangle - \left\langle \boldsymbol{\omega}_\perp{}^2 \frac{d^2}{dt^2}(\omega_\perp{}^2)\right\rangle. \end{aligned} \tag{D}$$

The coefficient of $t^6$ is related to the mean-square torque derivative term (the third) and also *four others* of the same dimension. Equation (5) gives the relation between $m_6$ and $K_2(0)$. Therefore $K_2(t)$ throughout its domain of existence $(t > 0)$ must reflect the time decay of all the vector terms on the right-hand side of (D), and is consequently an intricate function of time.

Differentiating equation (C) we have

$$\ddot{\boldsymbol{\omega}}_\perp = 2(\dot{\mathbf{u}} \times \dddot{\mathbf{u}}) + \mathbf{u} \times \ddddot{\mathbf{u}}, \tag{E}$$

giving

$$\left[\begin{aligned} &\langle \ddddot{\mathbf{u}}(0) \,.\, \ddddot{\mathbf{u}}(0)\rangle \\ &\quad \langle = \ddot{\boldsymbol{\omega}}_\perp{}^2\rangle - 2\langle \omega_\perp{}^8\rangle - 4\langle \omega_\perp{}^2(\ddot{\boldsymbol{\omega}})^2\rangle + 2\langle \dot{\boldsymbol{\omega}}_\perp{}^4\rangle + 10\left\langle \omega_\perp{}^2\left(\frac{d}{dt}(\omega_\perp{}^2)\right)^2\right\rangle \\ &\qquad - 9\left\langle \omega_\perp{}^4 \frac{d^2}{dt^2}(\omega_\perp{}^2)\right\rangle - 5\left\langle (\dot{\boldsymbol{\omega}}_\perp)^2 \frac{d^2}{dt^2}(\omega_\perp{}^2)\right\rangle \\ &\qquad - \tfrac{5}{4}\left\langle \left(\frac{d^2}{dt^2}(\omega_\perp{}^2)\right)^2\right\rangle + 3\left\langle \frac{d}{dt}(\omega_\perp{}^2)\left[\frac{d^3}{dt^3}(\omega_\perp{}^2) - \tfrac{3}{2}\frac{d}{dt}(\dot{\boldsymbol{\omega}}_\perp)^2\right.\right. \\ &\qquad \left.\left. - \tfrac{3}{2}\frac{d}{dt}(\boldsymbol{\omega}_\perp{}^4)\right]\right\rangle. \end{aligned}\right. \tag{F}$$

The coefficient $m_8$ is related to $K_3(0)$ by an equation such as (7).

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