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Realization of a hyperbolic secant memory function

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Abstract. We have derived a hyperbolic secant form of the memory function from the Mori equation of motion using a Markovian approximation and an *ansatz* for its higher-order memory function. The validity of the memory function has also been investigated.

The Mori integrodifferential equation [1] or motion has played a key role in the study of transport and dynamical properties of classical dense fluids. In this approach the fundamental theoretical quantity to be estimated is the memory function. Although there exist a microscopic formal expression for the memory function, it is not yet possible to calculate it exactly. Therefore, a number of phenomenological forms for it have been proposed [2, 3] in the literature without assigning a theoretical basis for it. In a series of papers [4–9] we have used a hyperbolic secant form of the memory function to calculate coefficients of self diffusion, shear viscosity, thermal conductivity and dynamical properties of dense fluids. This model has also been used by Heyes and Powles [10] to predict the transport coefficients of Lennard-Jones (LJ) fluids. Results of the model memory function coupled with microscopic sum rules have offered an interpretation of the transport coefficients [4–7] of LJ fluids over a wide range of densities and temperatures and also of dynamical properties of fluid argon [9] and a liquid metal [8] as was judged by their comparison with simulation and experimental data. Very recently the Mori equation of motion was solved analytically [11] using a sech(bt) form of the memory function. There its advantages over a Gaussian memory function and a simple exponential memory function are discussed. However, in all these studies the hyperbolic secant memory was used in a phenomenological sense, and hence the reason for its success in predicting transport coefficients is not yet fully understood. This could be achieved if the phenomenological form of the memory function is derived from its equation of motion which is the motivation of the present work. Therefore, in this paper we provide a theoretical formulation for realizing this memory function from the Mori equation of motion using two plausible approximations.

The time evolution of the time correlation function (TCF) $C(t)$ is obtained from the Mori equation of motion given as

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} + \int_0^t M_1(t-\tau)C(\tau)\,\mathrm{d}\tau = 0 \tag{1}$$

where $M_1(t)$ is the first-order memory function defined as

$$M_1(t) = \langle \dot{A}(0)\ \exp(\mathrm{i}(1-P))Lt\dot{A}(0)\rangle \tag{2}$$

with $A(t)$ as a dynamical variable of $C(t)$ such that

$$C(t) = \langle A(t)A(0)\rangle.$$

In equation (2), P and L are the projection and the Liouville operators, respectively. From the projection operator technique used in deriving equation (1), it can be shown that $M_1(t)$ and higher-order memory functions satisfy an equation similar to equation (1) so that

$$\frac{\mathrm{d}M_1(t)}{\mathrm{d}t} + \int_0^t M_1(t-\tau)M_1(\tau)\,\mathrm{d}\tau = 0 \tag{3}$$

and

$$\frac{\mathrm{d}M_2(t)}{\mathrm{d}t} + \int_0^t M_3(t-\tau)M_2(\tau)\,\mathrm{d}\tau = 0 \tag{4}$$

where $M_2(t)$ and $M_3(t)$ are the second- and third-order memory functions.

Defining the Fourier–Laplace transform given as

$$\tilde{f}(\omega) = \mathrm{i}\int_0^\infty \exp(\mathrm{i}\omega t)f(t)\,\mathrm{d}t \tag{5}$$

we rewrite equations (3) and (4) in the Fourier and Laplace space as

$$\tilde{M}_1(\omega) = -\frac{M_1(t=0)}{\omega + \tilde{M}_2(\omega)} \tag{6}$$

and

$$\tilde{M}_2(\omega) = -\frac{M_2(t=0)}{\omega + \tilde{M}_3(\omega)}. \tag{7}$$

Eliminating $\tilde{M}_2(\omega)$ from equations (6) and (7) we obtain

$$\tilde{M}_1(\omega)\omega^2 + M_1(t=0)\omega - M_2(t=0)\tilde{M}_1(\omega) + \tilde{M}_3(\omega)\big(\omega\tilde{M}_1(\omega) + M_1(t=0)\big) = 0. \tag{8}$$

On taking the inverse transform of the above equation, we obtain

$$\frac{\mathrm{d}^2M_1(t)}{\mathrm{d}t^2} + b^2M_1(t) + \int_0^t M_3(t-\tau)\frac{\mathrm{d}M_1(\tau)}{\mathrm{d}\tau}\,\mathrm{d}\tau = 0 \tag{9}$$

where $b^2 = M_2(t=0)$. The realization of the hyperbolic secant memory from equation (9) is based on two approximations. First, we use a Markovian approximation, i.e.

$$M_3(t-\tau) \to M_3(t) \tag{10}$$

which is based on the fact that the effect of the operator is to project out [12] the slowly varying properties of the system and, therefore, the Markovian approximation can easily be used for higher-order memory functions. Further, it has been recently suggested by Nettleton [13] that, by a suitable choice of the projection operator appearing in the definition of a memory function, one can obtain similar results for the correlation function obtained by using the Markovian approximation.

The second approximation introduces a closure for $M_3(t)$ which makes it depend on $M_1(t)$. The *ansatz* is

$$M_3(t) = AM_1^2(t) + BM_1(t) \tag{11}$$

where A and B are two coupling constants. This assumption is very similar to the assumption made by Götze [14] to describe the structural glass transition. Here, it may be noted that equation (11) is one stage higher than that of Götze's work. However, the nature of equation (1) preserves the idea of the feedback phenomena used in explaining supercooled liquids or glasses [15]. The physical background of the *ansatz* is the mode-coupling ideas in treating strongly interacting systems. Making use of equations (10) and (11) in equation (9), we obtain

$$\frac{\mathrm{d}^2M_1(t)}{\mathrm{d}t^2} - M_1(t)\big(Ba - b^2\big) + M_1^2(t)(B - Aa) + AM_1^3(t) = 0 \tag{12}$$

where $a = M_1(0)$. This is a non-linear equation for a conservative system. We have tried to solve this equation for $M_1(t)$ numerically for all possible choices of A and B. This analysis indicates the possibility of periodic solution [16] of the equation except for $A = B/a = 2b^2/a^2$, which on substituting in equation (12) gives

$$\frac{\mathrm{d}^2M_1(t)}{\mathrm{d}t^2} - b^2M_1(t) + \frac{2b^2}{a^2}M_1^3(t) = 0. \tag{13}$$

This equation is well known in non-linear dynamics and is exactly solvable with its solution given by

$$M_1(t) = a\ \mathrm{sech}(bt). \tag{14}$$

Thus we see that equation (13) whose solution is a hyperbolic secant function is derivable from the Mori equation of motion. Here, it may be noted that equation (14) satisfies the sum rules of the TCF up to fourth order, independent of choice of A and B. From equation (11) at $t = 0$ with $A = B/a = 2b^2/a^2$ we find that

$$M_3(0) = \big(2b^2/a^2\big)M_1^2(0) + \big(2b^2/a\big)M_1(0).$$

Noting that $M_1(0) = a$ and $b^2 = M_2(0)$ we find that

$$M_3(0) = 4b^2 = 4M_2(0) \tag{15}$$

where $M_n(0) = \delta_n$, are called the damping matrices and are related [17] to the sum rules of the TCF up to $2n$th order. Therefore, our approximation with $A = B/a = 2b^2/a^2$ predicts the sixth-order sum rule in terms of lower-order sum rules. Since δ_2 and δ_3 are known for the velocity autocorrelation function from theory [4] as well from the computer simulation studies [18, 19], equation (11) can be tested. The results obtained for $M_3(0)/M_2(0) = \delta_3/\delta_2$ are given in table 1 for various $T^* = k_BT/\epsilon$ and $n^* = n\sigma^3$; ϵ and σ are two parameters of LJ fluids. It is seen from the table that this ratio varies from 3.18 to 3.77 as against the predicted value of 4 from equation (15). This implies that hyperbolic secant memory not only preserves the sum rules up to fourth order exactly but also satisfies the sixth-order sum rule with a maximum error of about 25%.

To conclude, it is gratifying to see that a simple hyperbolic secant form of the memory function is derivable from the Mori equation of motion. This work puts our earlier work [4–9] on transport coefficients using the hyperbolic secant form of the memory function on a more theoretical footing. Further the derivation of equation (13) which is well known in non-linear dynamics widens the scope for the utility of the Mori equation of motion.

Table 1. Values of ratios δ_3/δ_2 obtained from molecular dynamics data of Lee and Chung [18]. The value in parentheses represents the MD value obtained by Toxvaerd [19].

n^*	T^*	δ_3/δ_2	n^*	T^*	δ_3/δ_2
0.85	0.727	3.18	0.75	5.122	3.71
0.85	0.778	3.37	0.65	1.457	3.31
0.85	4.76	3.69	0.65	1.430	3.30
0.85	4.66	3.70	0.65	5.084	3.61
0.75	1.104	3.26	0.65	5.026	3.66
0.75	5.267	3.68 (3.77)	0.30	1.575	3.28

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