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Analytic characteristics of time-correlation functions

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It is shown how the analytic properties of classical equilibrium time-autocorrelation functions (TACF's) and the corresponding memory functions (MF's), associated with the generalized Langevin equation in the Schmidt-orthogonalized representation, are intimately connected. In particular, the Maclaurin expansions of the TACF and Schmidt MF's and the continued-fraction representations of the corresponding Laplace transforms exist and converge in well-defined domains and under conditions consistent with the existence of finite positive transport coefficients.

I. INTRODUCTION

Many experimental measurements on relaxation processes, such as scattering cross sections, electromagnetic spectra, and thermal-transport coefficients, can be expressed as the Fourier transform of the time-autocorrelation function (TACF) of a characteristic dynamical variable. Consequently, TACF's (and their transforms) are central to the modern statistical-mechanical theory of irreversible processes.[1] Within classical mechanics, the *equilibrium* TACF of a dynamical variable A can be represented variously as

$$C(t) = \langle A(t)A^*(0)\rangle = \langle [\exp(\hat{\mathfrak{L}}t)A(0)]A^*(0)\rangle = \sum_{n=0}^{\infty}(-1)^n a_n t^{2n}/(2n)!\ , \tag{1}$$

where

$$a_n \equiv \langle [\hat{\mathfrak{L}}^n A(0)][\hat{\mathfrak{L}}^n A^*(0)]\rangle\ . \tag{2}$$

In (1) $\hat{\mathfrak{L}}$ is the Liouville operator in anti-Hermitian form and the brackets $\langle\cdots\rangle$ denote a full phase-space average with respect to the equilibrium distribution function. In addition, A is assumed to be an explicit function only of conjugate variables such as Cartesian coordinates and momenta. The a_n are the $2n$th moments of the Fourier transform of $C(t)$, i.e.,

$$a_n = \int_{-\infty}^{\infty} d\omega\, \omega^{2n}\tilde{C}(\omega)\ ,$$

where

$$\tilde{C}(\omega) = \pi^{-1}\int_0^{\infty} dt\, \cos(\omega t)C(t)\ .$$

Introducing Schmidt-orthogonalized variables Z_j defined by

$$Z_0(t) = A(t)\ ,$$

$$Z_j(t) = A_j(t) - \sum_{k=0}^{j-1}\left(\frac{\langle A_j(0)Z_k^*(0)\rangle}{\langle Z_k(0)Z_k^*(0)\rangle}\right)Z_k(t)\ ,$$

$$j = 1, 2, \ldots, N$$

and

$$A_j(t) = \hat{\mathfrak{L}}^j A(t)$$

leads to the following generalized Langevin-type equation of motion for $C(t)$[2-5]:

$$\dot{C}(t) = C_1(t)\ , \tag{3a}$$

$$\dot{C}_j(t) = C_{j+1}(t) - \lambda_j C_{j-1}(t)\ , \quad 1 \leq j \leq N-1 \tag{3b}$$

$$C_N(t) = -\lambda_N \int_0^t d\tau\, K_N(\tau)C_{N-1}(t-\tau)\ , \tag{3c}$$

where

$$C_j(t) \equiv \langle Z_j(t)Z_0^*(0)\rangle\ , \tag{4a}$$

$$\lambda_j \equiv \langle Z_j(0)Z_j^*(0)\rangle\langle Z_{j-1}(0)Z_{j-1}^*(0)\rangle^{-1}\ , \quad j \geq 1 \tag{4b}$$

and

$$K_N(\tau) \equiv \langle\{\exp[(1-\hat{P}_N)\hat{\mathfrak{L}}\tau]Z_N(0)\}Z_N^*(0)\rangle \times \langle Z_N(0)Z_N^*(0)\rangle^{-1}\ . \tag{4c}$$

The memory function (MF) $K_N(t)$ is the TACF of Z_N evolving under the projected Liouville operator; $\hat{P}_N$ projects any dynamical function onto the manifold spanned by $Z_0, Z_1, \ldots, Z_{N-1}$.

Since the "lowering coefficients" λ_j [see (3b)] are uniquely determined by the moments a_n [see (2)], and conversely, $C(t)$ can be regarded as a functional of the set $\Lambda = \{\lambda_j\}_{j=1}^{\infty}$. Likewise, $K_N(t)$ is the same functional of its lowering coefficients, say $\{\mu_j^{(N)}\}_{j=1}^{\infty}$. In the next section we shall prove the relation

$$\mu_j^{(N)} = \lambda_{j+N}\ . \tag{5}$$

The significance of (5) is that analytic properties of $C(t)$ depending only upon the asymptotic (i.e., large j) behavior of λ_j are also shared by $K_N(t)$. The purpose of this article is to elucidate some of the consequences of this observation. Thus, in Sec. III we shall examine the influence of the asymptotic behavior of λ_j upon the convergence properties of the Maclaurin representations (MR's) of $C(t)$ and $K_N(t)$ and in Secs. IV and V we shall do the same for the infinite continued-fraction representations (ICFR's) of the Laplace transforms of C and K_N. Next in Sec. VI we shall develop some of the practical implications of the results of previous sections by deriving conditions on the lowering coefficients necessary for the existence of positive finite transport coefficients.

II. RELATION BETWEEN LOWERING COEFFICIENTS FOR $C(t)$ AND $K_N(t)$

In this section we wish to prove relation (5). Taking the Laplace transform of (3) gives

$$s\overline{C}(s) - C(0) = \overline{C}_1(s)\,,$$
$$s\overline{C}_j(s) + \lambda_j \overline{C}_{j-1}(s) = \overline{C}_{j+1}(s)\,, \quad 1 \le j \le N-1$$

and

$$\overline{C}_N(s) = -\lambda_N \overline{K}_N(s)\overline{C}_{N-1}(s)\,, \tag{6}$$

where the overbar denotes the transformed function. Defining the ancillary functions

$$G_k(s) \equiv \overline{C}_k(s)/\overline{C}_{k-1}(s)\,,$$

permits us to rewrite (6) as

$$\overline{C}(s) = C(0)\,[s - G_1(s)]^{-1}\,,$$
$$G_j(s) = -\lambda_j [s - G_{j+1}(s)]^{-1}\,, \quad 1 \le j \le N-1$$

and

$$G_N(s) = -\lambda_N \overline{K}_N(s)\,. \tag{7}$$

Successive elimination of G_k, beginning with the last line of (7), yields the (finite) continued-fraction representation of $\overline{C}(s)$:

$$\overline{C}(s)/C(0) = \frac{1}{s+}\,\frac{\lambda_1}{s+}\,\frac{\lambda_2}{s+}\cdots\frac{\lambda_{N-2}}{+\;s\;+}\,\frac{\lambda_{N-1}}{[s+\lambda_N\overline{K}_N(s)]}\,. \tag{8}$$

Comparing (8) to the ICFR[3,6] of $\overline{C}(s)$,

$$\overline{C}(s)/C(0) = \frac{1}{s+}\,\frac{\lambda_1}{s+}\,\frac{\lambda_2}{s+}\cdots\frac{\lambda_{N-1}}{+\;s\;+}\,\frac{\lambda_N}{s}+\cdots\,, \tag{9}$$

we find

$$\overline{K}_N(s) = \frac{1}{s+}\,\frac{\lambda_{N+1}}{s\;+}\,\frac{\lambda_{N+2}}{s\;+}\cdots\frac{\lambda_{N+j}}{+\;s\;+}\cdots\,. \tag{10}$$

Since $K_N(t)$ is the TACF of the dynamical variable Z_N (governed by the projected Liouville operator), its Laplace transform has the ICFR

$$\overline{K}_N(s)/K_N(0) = \frac{1}{s+}\,\frac{\mu_1^{(N)}}{s\;+}\,\frac{\mu_2^{(N)}}{s\;+}\cdots \frac{\mu_j^{(N)}}{+\;s\;+}\cdots\,, \tag{11}$$

in which the $\mu^{(N)}$'s are lowering coefficients that play the same role with respect to $K_N(t)$ as do the λ's with respect to $C(t)$. Comparing (10) with (11) and noting from (4c) that $K_N(0) = 1$ we obtain finally relation (5).

The significance of (5) is readily understood. From (9) and (11) it is evident that the mathematical properties of $\overline{C}(s)$ and of $\overline{K}_N(s)$ (and, consequently, of their Laplace inverses) are determined by the lowering coefficients. Furthermore, every property of $\overline{C}(s)$ [or $C(t)$] depending only upon the asymptotic (i.e., large j) behavior of λ_j must also be a property of $\overline{K}_N(s)$ [or $K_N(t)$].

III. CONVERGENCE PROPERTIES OF THE MACLAURIN REPRESENTATIONS OF C AND K_N

We may conveniently classify the asymptotic behavior of the lowering coefficients by the "order of infinity" of the sequence $\Lambda = \{\lambda_j\}_{j=1}^{\infty}$. Consequently, those analytic properties of C and K_N depending only on the asymptotic behavior of λ_j can also be categorized by the order of infinity. In this section we examine some of these properties for the Maclaurin expansions (MR's) of $C(t)$ and $K_N(t)$.

By the term "order of infinity" we shall mean the following. If the inequality[7]

$$m \le \lim_{j\to\infty} \lambda_j / j^p \le M$$

holds for positive finite numbers m and M, then λ_j is of the order of j^p and we write $\lambda_j = O(j^p)$. If M must be chosen infinite then we write $\lambda_j > O(j^p)$, whereas if m must be chosen zero we write $\lambda_j < O(j^p)$. In the case $\lambda_j = O(j^p)$ there exist finite positive numbers m_1 and M_1 such that $0 < m_1 \le m$, $M_1 \ge M$, and

$$m_1 \le \lambda_j / j^p \le M_1\,, \quad \text{all } j\,. \tag{12}$$

From (5) it follows that

$$m_1 \le \mu_j^{(N)}/(j+N)^p \le M_1\,, \quad \text{all } j\,,$$

if $\lambda_p = O(j^p)$.

It can be shown[8] that the moment a_n of a classical equilibrium TACF is a sum of $Q_n = (2n)!\,[n!\,(n+1)!]^{-1}$ positive terms of the form

$$\lambda_1^{k_1}\lambda_2^{k_2}\lambda_3^{k_3}\cdots\lambda_J^{k_J}\,,$$

where J ranges from 1 to n and

$$\sum_{i=1}^{J} k_i = n\,, \quad k_i \ge 1\,.$$

Thus, if $\lambda_j = O(j^p)$ then

$$|(-1)^n a_n t^{2n}/(2n)!\,| < M_1^n (n!\,)^p Q_n t^{2n}/(2n)! \equiv \rho_n\,. \tag{13}$$

Similarly, the magnitude of the $(n+1)$th term of the MR of $K_N(t)$ is less than

$$\rho_n^{(N)} \equiv M_1^n [(N+n)!\,]^p Q_n t^{2n} / [(2n)!(N!)^p]\,. \tag{14}$$

Using Stirling's asymptotic formula for $n!$, we find from (13) and (14) that

$$\lim_{n\to\infty}(\rho_n)^{1/n}=\lim_{n\to\infty}(\rho_n^{(N)})^{1/n}$$

$$=\lim_{n\to\infty}M_1t^2\exp(2-p)n^{p-2}\,.$$

It then follows from the root test for absolute convergence of a series[9] that the MR's of $C(t)$ and of $K_N(t)$ are absolutely convergent if $\lambda_j< O(j^2)$, divergent if $\lambda_j> O(j^2)$, and absolutely convergent for $t<M_1^{-1/2}$ if $\lambda_j=O(j^2)$.

The radius of convergence R of the MR of $C(t)$ can be written[10]

$$R=\lim_{n\to\infty}\left|(-1)^n a_n/(2n)!\right|^{-1/2n}.$$

Now, if $\lambda_j=O(j^p)$, we have from (12)

$$m_1^n(n!)^p/(2n)!<\left|(-1)^n a_n/(2n)!\right| <M_1^nQ_n(n!)^p/(2n)!\ . \tag{15}$$

Inequality (15) provides upper and lower bounds R_u and R_l on R as

$$R_u=\lim_{n\to\infty}[m_1^n(n!)^p/(2n)!]^{-1/2n}$$

and

$$R_l=\lim_{n\to\infty}[M_1^n(n!)^p/\{n!(n+1)!\}]^{-1/2n}.$$

Again with the aid of Stirling's approximation we obtain

$$R_u=\lim_{n\to\infty}2m_1^{-1/2}\exp[(p/2)-1]n^{(1-p/2)}$$

and

$$R_l=\lim_{n\to\infty}M_1^{-1/2}\exp[(p/2)-1]n^{(1-p/2)}\,.$$

The analogous calculation for the MR of $K_N(t)$ gives

$$R_u^{(N)}=\lim_{n\to\infty}2m_1^{-1/2}\exp[(p/2)-1](n+N)^{-p/2}n$$

and

$$R_l^{(N)}=\lim_{n\to\infty}M_1^{-1/2}\exp[(p/2)-1](n+N)^{-p/2}n\,.$$

Thus, if $p<2$, $R_l=R_l^{(N)}=\infty$, whereas if $p=2$,

$$M_1^{-1/2}\leq R\leq 2m_1^{-1/2}\,, \tag{16}$$

and if $p>2$, then $R_u=R_u^{(N)}=0$. Therefore, we have the following result.

Statement (I). The MR's *of $C(t)$ and $K_N(t)$ have infinite radii of convergence if $\lambda_j<O(j^2)$, finite nonzero radii if $\lambda_j=O(j^2)$, and vanishing radii if $\lambda_j>O(j^2)$.*

Thus, $C(t)$ and $K_N(t)$ are regular at the origin when $\lambda_j\leq O(j^2)$.

To illustrate the quality of the bounds on R given by (16) for the case $\lambda_j=O(j^2)$, we consider the functions $C_s(t)=\operatorname{sech}(t)$ and $C_L(t)=(1+t^2)^{-1}$. In both cases $p=2$. For $C_s(t)$ one has $\lambda_j=j^2$ (Ref. 11), hence, $m_1=M_1=1$ and $1\leq R\leq 2$. This result compares favorably with the exact value $R=\pi/2$. For $C_L(t)$ a numerical study[8] yields $m_1=2$, $M_1=2.5$ so that $0.63\leq R\leq 1.42$. Again, the bounds compare reasonably well with the exact value of unity.

We note that a convergent power series with $R>0$ is uniformly convergent for $|t|<R$. Hence, the MR's of $C(t)$ and $K_N(t)$ are uniformly convergent for $|t|\leq R_l$. Moreover, our criteria for convergence are based on the root test. More sophisticated criteria may yield more refined bounds on the radius of convergence. For example, $j^2\ln j>O(j^2)$ by our definition. But also $j^2\ln j<O(j^{2+\epsilon})$ for any positive ϵ, no matter how small. Consequently, the transition from $O(j^2)$ to greater than $O(j^2)$ must be treated carefully.

IV. ANALYTIC PROPERTIES OF $\bar{C}(s)$ AND $\bar{K}_N(s)$

An amalgamation of several theorems from the analytic theory of continued fractions,[3,11] specialized to the ICFR of $\bar{C}(s)$ given by (9), states that (9) converges uniformly in every bounded region of the complex s-plane whose distance from the imaginary s-axis is positive if, and only if, the ICFR of $\bar{C}(s)$ satisfies the Hamburger condition, which can be expressed in the present context as follows. Let

$$\begin{aligned} &b_1=1\,,\\ &b_{2k+1}=(\lambda_1\lambda_3\lambda_5\cdots\lambda_{2k-1})(\lambda_2\lambda_4\lambda_6\cdots\lambda_{2k})^{-1}\,,\\ &b_2=\lambda_1^{-1}\,,\\ &b_{2k}=b_{2k-1}^{-1}\lambda_{2k-1}^{-1}; \end{aligned} \tag{17}$$

then either

$$B_{\text{even}}\equiv\sum_{k=1}^{\infty}b_{2k} \tag{18a}$$

or

$$B_{\text{odd}}\equiv\sum_{k=0}^{\infty}b_{2k+1} \tag{18b}$$

or

$$B\equiv\sum_{k=0}^{\infty}b_{2k+1}(b_2+b_4+\cdots+b_{2k})^2 \tag{18c}$$

diverges. If the Hamburger condition holds, i.e., if at least one of (18a), (18b), or (18c) holds, then the ICFR of $\bar{C}(s)$ is analytic in the half-plane $\mathrm{Re}(s)>0$. If the Hamburger condition does not hold, the ICFR of $\bar{C}(s)$ diverges for every value of s.

We may, in the present context, dispense with (18c) by appealing to a theorem of Van Vleck,[11] which asserts that (9) converges for $\mathrm{Re}(s)>0$ if, and only if, the infinite series $\sum_{k=1}^{\infty}|b_k|$ diverges, *provided* that

$$\mathrm{Re}(b_1 s) > 0 \quad \text{and} \quad |\mathrm{Im}(b_k s)| \leq c\,\mathrm{Re}(b_k s) \tag{19}$$

for $k = 1, 2, 3 \ldots$ and $c > 0$. In the present case $b_k > 0$ so that $\sum_{k=1}^{\infty} |b_k| = B_{\text{even}} + B_{\text{odd}}$. Since $\lambda_k > 0$, the provisos (19) are satisfied for $\mathrm{Re}(s) > 0$ and $\sum_{k=1}^{\infty} |b_k|$ diverges if, and only if, at least one of B_{even} or B_{odd} diverges. An alternative approach is to demonstrate that (18c) diverges if, and only if, at least one of (18a) and (18b) holds under conditions (19).

Statement (II). We shall first demonstrate that: *The* ICFR *of* $\overline{C}(s)$ *converges if, and only if, that of* $\overline{K}_N(s)$ *does.*

The Hamburger condition for $\overline{K}_N(s)$ can be expressed as follows:

$$B_{\text{even}}^{(N)} = \begin{cases} (\lambda_2\lambda_4 \cdots \lambda_{N-1})(\lambda_1\lambda_3 \cdots \lambda_N)^{-1} \sum_{k=n}^{\infty} b_{2k+1}, & N = 2n-1 \\ (\lambda_1\lambda_3 \cdots \lambda_{N-1})(\lambda_2\lambda_4 \cdots \lambda_N)^{-1} \sum_{k=n+1}^{\infty} b_{2k}, & N = 2n \end{cases} \tag{20a}$$

$$B_{\text{odd}}^{(N)} = \begin{cases} (\lambda_1\lambda_3 \cdots \lambda_N)(\lambda_2\lambda_4 \cdots \lambda_{N-1})^{-1} \sum_{k=n}^{\infty} b_{2k}, & N = 2n-1 \\ (\lambda_2\lambda_4 \cdots \lambda_N)(\lambda_1\lambda_3 \cdots \lambda_{N-1})^{-1} \sum_{k=n}^{\infty} b_{2k+1}, & N = 2n . \end{cases} \tag{20b}$$

Note that the infinite sums in (20) correspond to B_{even} or B_{odd} minus a finite number of terms. Consequently, $B_{\text{even}}^{(N)}$ and/or $B_{\text{odd}}^{(N)}$ diverges, if at least one of B_{even} or B_{odd} does, and conversely. Invoking the theorem of Van Vleck[11] completes the proof of statement (II).

Statement (III). Combining statement (II) with the theorems stated earlier, we conclude that: *The* ICFR *of* $\overline{C}(s)$ *converges uniformly to a holomorphic function in the half-plane* $\mathrm{Re}(s) > 0$ *if, and only if, the same is true for* $\overline{K}_N(s)$.

V. CONVERGENCE CRITERIA FOR $\overline{C}(s)$ AND $\overline{K}_N(s)$

Here we shall examine how the Hamburger criteria (18a) and (18b) constrain the behavior of the sequence of lowering coefficients $\Lambda = \{\lambda_k\}_{k=1}^{\infty}$. Let us begin by supposing that Λ has a finite least upper bound λ_{lub}. Then from (17) we have

$$b_{2k} = b_{2k-1}^{-1}\lambda_{2k-1}^{-1} \geq b_{2k-1}^{-1}\lambda_{\text{lub}}^{-1} > 0 . \tag{21}$$

Now, if B_{even} converges, $b_{2k} \sim 0$ at large k and it follows from (21) that $b_{2k-1}^{-1} \sim 0$ in this same limit. This implies that b_{2k-1} diverges as k becomes large and consequently, that B_{odd} diverges. If, on the other hand, B_{even} diverges, we need not examine B_{odd}.

Statement(IV). We conclude that: *If* Λ *has a finite least upper bound, then the* ICFR *of* $\overline{C}(s)$ *converges.*

Note that on account of the positivity of the λ's, Λ is bounded below by zero. Thus, Λ is a bounded infinite sequence so that it has at least one accumulation point.[12]

This last point is of particular significance in connection with crystalline solids, for which the phonon frequency-distribution function $g(\omega)$ possesses cutoffs.[13] For pure, cubic lattices $g(\omega)$ is the Fourier transform of the single-particle velocity TACF, $\phi(t)$.[14] Cutoffs in $g(\omega)$ translate into bounds on the λ's associated with $\phi(t)$. Indeed, frequency-bounding approximations on $g(\omega)$ have been used[15,16] to construct functions that bound $\phi(t)$. This technique is also applicable to fluids.

Let us consider now the situation in which

$$\lim_{k\to\infty} \lambda_{k+1}/\lambda_k > 1 . \tag{22}$$

Condition (22) implies that Λ has no finite accumulation points. There exists an integer n and a real number $\mu > 1$ such that

$$\lambda_{k+1}/\lambda_k > \mu , \quad \text{all } k > n . \tag{23}$$

In case n is even, i.e., $n = 2m$, we have from (17) and (23)

$$b_{2k} < h_m \lambda_{2m+1}^{-1} \mu^{m+1} \nu^k , \quad k > m \tag{24}$$

where

$$h_m \equiv (\lambda_2\lambda_4 \cdots \lambda_{2m})(\lambda_1\lambda_3 \cdots \lambda_{2m-1})^{-1} \tag{25}$$

and

$$\nu \equiv \mu^{-1} < 1 .$$

Thus, it follows from (18a) and (24) that

$$B_{\text{even}} < \sum_{k=1}^{m} b_{2k} + h_m \lambda_{2m+1}^{-1} \mu^{m+1} \sum_{k=m+1}^{\infty} \nu^k . \tag{26}$$

Since the right-hand member of (26) is bounded and since the partial sums to B_{even} increase monotonically, B_{even} converges. In case n is odd, i.e., $n = 2m+1$, we find that

$$b_{2k+1} < h_m^{-1} \mu^m \nu^k , \quad k > m$$

and by a logical sequence analogous to the preceding one we conclude that B_{odd} converges. Therefore, by Van Vleck's theorem[11] it follows that the ICFR fails to converge if (22) holds. Hence, if Λ has at most a single accumulation point, then a *necessary* condition for the convergence of the ICFR of $\overline{C}(s)$ is

$$\lim_{k\to\infty} \lambda_{k+1}/\lambda_k \leq 1 . \tag{27}$$

Now let us consider the case

$$\lim_{k\to\infty} \lambda_{k+1}/\lambda_k < 1 . \quad (28)$$

Condition (28) implies the existence of an integer n and a real number $\mu < 1$ such that

$$\lambda_{k+1}/\lambda_k < \mu , \quad \text{all } k > n . \quad (29)$$

From (29) it follows that

$$\lambda_{n+m} < \mu^m \lambda_n , \quad m = 0, 1, 2, \ldots .$$

Thus, Λ is bounded above by

$$\lambda_{\text{lub}} = \max\{\lambda_1, \lambda_2, \ldots, \lambda_n\}$$

and from statement (IV) we conclude the following.

Statement (*V*). *The* ICFR *of* $\bar{C}(s)$ *converges under condition* (28).

Note that statement (V) is somewhat stronger than the result which is reached upon the basis of the ratio test[9] applied to B_{even} or B_{odd}. The ratio test would require at least one of the following conditions as sufficient for the convergence of the ICFR of $\bar{C}(s)$:

$$\lim_{k\to\infty} \lambda_{2k}/\lambda_{2k-1} < 1 , \quad (30a)$$

$$\lim_{k\to\infty} \lambda_{2k+1}/\lambda_{2k} < 1 . \quad (30b)$$

To deepen our understanding of the results thus far obtained, we consider the special case

$$\lambda_k = \begin{cases} ak^p, & k \text{ even} \\ bk^p, & k \text{ odd} \end{cases} \quad (31)$$

where $a \neq b$ and $a, b > 0$. We have

$$\lambda_{2k}/\lambda_{2k-1} \sim ab^{-1}[1 + p/(2k-1)] + O(k^{-2}). \quad (32a)$$

$$\lambda_{2k+1}/\lambda_{2k} \sim a^{-1}b(1 + p/2k) + O(k^{-2}) . \quad (32b)$$

In this case Λ has no accumulation points, although the sequence of ratios $\{\lambda_{k+1}/\lambda_k\}_{k=1}^{\infty}$ has two, namely ab^{-1} and $a^{-1}b$. Clearly (30) fails to apply. Calculating the b's asymptotically from (17) and (32), we obtain

$$b_{2k+1} \sim b_{2k'+1}(k/k')^{-bp/2a} \exp[(b-a)(k-k')/a] , \quad (33a)$$

$$b_{2k} \sim b_{2k'}(k/k')^{-ap/2b} \exp[(a-b)(k-k')/b] , \quad (33b)$$

where k' is chosen sufficiently large. Since $a \neq b$, at least one of (33) diverges exponentially with k for *all* values of p. Hence, either B_{even} or B_{odd} diverges for all values of p and the ICFR of $\bar{C}(s)$ converges. The lowering coefficients of the Jacobian elliptic functions $cn(t,k)$ and $dn(t,k)$ are of the form (31).[11]

It is interesting that in case $a = b$, then either B_{odd} or B_{even} diverges only if $p \leq 2$. We shall treat this case more fully later.

Next, consider the case

$$\lim_{k\to\infty} \lambda_{k+1}/\lambda_k = 1 . \quad (34)$$

We shall show in Sec. V that condition (34) is *necessary* for the existence of a positive finite transport coefficient. Thus, this case is of considerable relevance physically; it is also interesting from a purely mathematical viewpoint since the ratio test fails.

We first develop a bound on the rate of change of the lowering coefficient with respect to its index. Define

$$p_k \equiv (\lambda_{k+1}/\lambda_k) - 1 , \quad k = 0, 1, 2, \ldots \quad (35)$$

where we take $\lambda_0 = \lambda_1$. Thus from (34) it follows that

$$\lim_{k\to\infty} p_k = 0 ,$$

and from the positivity of the λ's that

$$p_k > -1 , \quad \text{all } k .$$

Moreover,

$$\lambda_{k+1} = \lambda_1 \prod_{l=1}^{k+1} (1 + p_l) .$$

In the limit of large k we can solve (35) to get

$$\lambda_k \sim \lambda_{k'} \exp\left(\sum_{l=k'}^{k} p_l\right), \quad k \geq k'$$

for k' sufficiently large. Since the sequence $\{p_l\}_{l=1}^{\infty}$ is bounded above,

$$\lim_{k\to\infty} k^{-1} \sum_{l=k'}^{k} |p_l| \leq M , \quad (36)$$

where M is some finite positive number. Hence, from (36) we conclude that if (34) holds

$$\lambda_k \sim \lambda_{k'} \exp[C(k)] ,$$

where $|C(k)| \leq \mathcal{O}(k)$, i.e., under condition (34) the lowering coefficients cannot increase faster than exponentially with k.

If the series $\sum_{l=1}^{\infty} |p_l|$ converges, the sequence Λ is bounded above and it follows by statement (IV) that the ICFR of $\bar{C}(s)$ converges. If, however, $p_{2l+1} \leq 0$ for all $l > l'$, then

$$b_{2l+2}/b_{2l} = \lambda_{2l}/\lambda_{2l+1} = (1 + p_{2l+1})^{-1} \geq 1 , \quad \text{all } l > l' .$$

Hence, $b_{2l+2} > b_{2l}$, for all $l > l'$, B_{even} diverges and the ICFR of $\bar{C}(s)$ converges. By similar reasoning, if $p_{2l} \leq 0$ for all $l > l'$, then B_{odd} diverges and the ICFR of $\bar{C}(s)$ converges. Combining these results, we conclude that the ICFR of $\bar{C}(s)$ converges under condition (34) and at least one of the following additional conditions:

(a) $\sum_{l=1}^{n} |p_l|$ converges,
(b) $p_{2l} \leq 0$ for all $l > l'$,
(c) $p_{2l+1} \leq 0$ for all $l > l'$,

where l' is some fixed integer. Of course, if $p_l = 0$ for all $l > l'$, then B_{odd} always diverges [see (17)].

Finally, let us assume that

$$\lambda_{k+1}/\lambda_k = 1 + p/k + o(k^{-1}), \quad k \text{ large}, \tag{37}$$

where p is a constant independent of k. From (17) we deduce that

$$b_{2k+1} - b_{2k-1} = (-p/2k) b_{2k-1} + o(k^{-1}), \tag{38a}$$

$$b_{2k+1} - b_{2k} = (-p/2k) b_{2k} + o(k^{-1}). \tag{38b}$$

Integrating (38), we find

$$b_{2k+1} \sim b_{2k'+1}(k/k')^{-p/2} \sim k^{-p/2}, \tag{39a}$$

$$b_{2k} \sim b_{2k'}(k/k')^{-p/2} \sim k^{-p/2}, \tag{39b}$$

for k greater than some sufficiently large fixed k'. We conclude from (39) that both B_{even} and B_{odd} diverge if $p \leq 2$. Consequently, statement (VI) holds true.

Statement (VI). Under condition (37), the ICFR *of* $\bar{C}(s)$ *converges if* $p \leq 2$.

We note an interesting connection between statements (VI) and (I) (see Sec. III). If λ_k is of order p, i.e., if (37) holds, then $p = 2$ is a sort of "singular" point. For $p < 2$, the MR's of $C(t)$ and $K_N(t)$ have infinite radii of convergence and the ICFR's of $\bar{C}(s)$ anf $\bar{K}_N(s)$ converge for all s in the half-plane Re $(s) > 0$. On the other hand, if $p > 2$ the radii of convergence vanish and the ICFR's fail to converge.

In closing this section we consider a generalization of (37), namely,

$$\lambda_{2k}/\lambda_{2k-1} = 1 + p/2k + O(k^{-1}), \tag{40a}$$

$$\lambda_{2k+1}/\lambda_{2k} = 1 + q/2k + O(k^{-1}), \quad \text{large } k. \tag{40b}$$

Condition (40) appears to obtain in the case of a Lorentzian TACF $(1 + \beta^2 t^2)^{-1}$, for example.[8] Equations (40) can be rewritten as

$$\lambda_{2k} - \lambda_{2k-1} = (p/2k)\lambda_{2k-1} + o(k^{-1}), \tag{41a}$$

$$\lambda_{2k+1} - \lambda_{2k} = (q/2k)\lambda_{2k} + o(k^{-1}). \tag{41b}$$

Combining (41), we obtain to $o(k^{-1})$,

$$\lambda_{2k+2} - \lambda_{2k} = [(p+q)/2k]\lambda_{2k}, \tag{42a}$$

$$\lambda_{2k+1} - \lambda_{2k-1} = [(p+q)/2k]\lambda_{2k-1}, \quad \text{large } k. \tag{42b}$$

Equations (42) can be solved to yield

$$\lambda_k = \lambda_{k'}(k/k')^{(p+q)/2}, \quad k > k'$$

for k' sufficiently large. We conclude that if $p + q \leq 4$, then $\lambda_k \leq O(k^2)$; from statement (I) it follows that $C(t)$ and $K_N(t)$ are regular at the origin $t = 0$. For k' sufficiently large we calculate

$$b_{2k+2} \sim b_{2k'+2}(k/k')^{-q/2},$$

$$b_{2k+1} \sim b_{2k'+2}(k/k')^{-p/2}, \quad k \geq k'.$$

Therefore, the ICFR of $\bar{C}$ converges if *either* p *or* q is less than or equal to 2. That is, the ICFR of $\bar{C}$ converges if, for instance, $p \leq 2$, regardless of the value of q. But the MR has a nonzero radius of convergence only if $p + q \leq 4$. Hence, the condition for the existence of the MR is much more stringent than that for the existence of the ICFR. The case (40) emphasizes the nonequivalence of the analytic characteristics of the MR and ICFR.

VI. CONNECTION WITH TRANSPORT COEFFICIENTS

The results of the preceding section are largely just straightforward exercises in the analytic theory of continued fractions. To demonstrate their relevance to physics, we shall consider here the zero-frequency transport integral

$$D = \int_0^\infty dt\, C(t),$$

which provides a characteristic time for the physical process of interest.

If the ICFR of $\bar{C}(s)$ converges, D is given[17] by

$$D = \lim_{k\to\infty} d_{2k}(f_{k-1}/g_k)^{1/2}$$

$$= \lim_{k\to\infty} d_{2k+1}(f_k/g_k)^{1/2}, \tag{43}$$

where

$$f_k = 1 + \sum_{l=1}^{k}\left(\prod_{m=l}^{k} \lambda_{2m+1}/\lambda_{2m}\right), \tag{44a}$$

$$g_k = 1 + \sum_{l=1}^{k}\left(\prod_{m=l}^{k} \lambda_{2m}/\lambda_{2m-1}\right), \tag{44b}$$

$$d_{2k} = h_k \lambda_{2k}^{-1/2}, \tag{45a}$$

$$d_{2k+1} = h_k \lambda_{2k+1}^{-1/2}, \tag{45b}$$

and h_k is defined by (25).

Suppose, in addition, that D is positive and finite. Then, taking the ratio of the last line of (43) to the first line, we obtain

$$\lim_{k\to\infty} f_k/(\lambda_{2k+1} f_{k-1}/\lambda_{2k}) = 1. \tag{46}$$

From (44a) one may readily obtain the identity

$$f_k - 1 = \lambda_{2k+1} f_{k-1}/\lambda_{2k}, \tag{47}$$

which upon substituting into (46) yields

$$\lim_{k\to\infty} \frac{1}{1 - 1/f_k} = 1. \tag{48}$$

Since $f_k > 0$ for all k it follows from (48) that

$$\lim_{k\to\infty} f_k = \infty.$$

If we compute the ratio of the first line of (43) (with $k+1$ in place of k) to the second line, we obtain

$$\lim_{k\to\infty} g_k/(\lambda_{2k+1} g_{k+1}/\lambda_{2k+2}) = 1 .$$

The analog of (47) is found from (44b) to be

$$g_{k+1} - 1 = \lambda_{2k+2} g_k/\lambda_{2k+1} .$$

Therefore,

$$\lim_{k\to\infty}(1 - 1/g_{k+1}) = 1 ,$$

which implies that

$$\lim_{k\to\infty} g_k = \infty .$$

In summary, we conclude the following.

Statement (VII). If the ICFR *of* $\overline{C}(s)$ *converges then a necessary condition for* $0<D<\infty$ *to hold is that both* f_k *and* g_k *diverge as* $k\to\infty$.

Define the numbers α_l by

$$\alpha_l \equiv \ln(\lambda_{l+1}/\lambda_l) ,$$

and suppose that

$$\lim_{j\to\infty} \lambda_{j+1}/\lambda_j < 1 .$$

Then there exists an integer L and a real number μ such that

$$\alpha_{2l+1} \leqslant \mu < 0 , \quad l > L . \tag{49}$$

Then, for $k>L$, we have from (44a)

$$f_k = 1 + \sum_{j=L+1}^{k} \exp\left(\sum_{l=j}^{k} \alpha_{2l+1}\right) + U_L(k) ,$$

where

$$U_L(k) \equiv \sum_{j=1}^{L} \exp\left(\sum_{l=j}^{k} \alpha_{2l+1}\right) .$$

From (49) it follows that $U_L(k)$ is a monotonically decreasing function of k for $k>L$. Therefore,

$$0 < U_L(k) < U_L(L) , \quad k > L .$$

Since $\exp(\alpha_{2l+1}) \leqslant \exp(\mu)$, $l>L$, we conclude that

$$1 < f_k < U_L(L) + [1 - \exp(\mu)]^{-1} , \quad k > L$$

and consequently that f_k is bounded. By a parallel argument we conclude that g_k is also bounded. Summarizing these results, we see that a *necessary* condition for the divergence of f_k and g_k is

$$\lim_{j\to\infty} \lambda_{j+1}/\lambda_j \geqslant 1 . \tag{50}$$

However, we have shown earlier that (27) is a necessary condition for the convergence of the ICFR of $\overline{C}(s)$, which we have assumed. Thus, (50) must be amended to read

$$\lim_{j\to\infty} \lambda_{j+1}/\lambda_j = 1 , \tag{51}$$

and we conclude finally the following.

Statement (VIII). In the case of at most a single accumulation point in Λ *(51) is necessary for the existence of a finite, positive transport integral.*

We emphasize the "one-way" nature of statement (VIII), i.e., (51) is not sufficient to guarantee the positivity of transport coefficients. For example, in case $\lambda_{2k} = 2k-1$ and $\lambda_{2k+1} = 2k+1$, (51) holds and the ICFR of $\overline{C}(s)$ converges, yet $D=0$ by direct calculation from (43).

Finally, consider the following special case of multiple accumulation points in Λ:

$$\lambda_k = \begin{cases} a, & k \text{ even} \\ b, & k \text{ odd} \end{cases} . \tag{52}$$

Since λ_k is bounded, the ICFR of $\overline{C}(s)$ converges. From (44) and (45) we compute

$$d_{2k} = (a/b)^k a^{-1/2} ,$$

$$d_{2k+1} = (a/b)^k b^{-1/2} ,$$

$$f_k = [1 - (b/a)^{k+1}]/(1 - b/a) ,$$

$$g_k = [1 - (a/b)^{k+1}]/(1 - a/b) .$$

If $a>b$, D diverges to ∞ as $(a/b)^{k/2}$. When $a<b$, D diverges to zero as $(a/b)^{k/2}$. Since one of f_k or g_k converges if $a\neq b$, it is reasonable that D is either zero or finite. Note that (52) is a special case of (31).

VII. SUMMARY AND DISCUSSION

This article has reached two principal results. The first is relation (5) between the lowering coefficients of the TACF $C(t)$ and its associated Nth Schmidt memory function $K_N(t)$, which is itself the TACF of the variable Z_N evolving under the projected Liouville operator [see (4c)]. Since TACF's are functionals of their moments, or equivalently, of their lowering coefficients, (5) relates the analytic properties of $C(t)$ and $K_N(t)$ if only implicitly. Indeed, we derived some of these properties depending only on the asymptotic behavior of the λ's. Thus, we showed in Sec. III that the Maclaurin expansions of $C(t)$ and $K_N(t)$ are regular at the origin if $\lambda_j \leqslant O(j^2)$, and in Sec. IV that the infinite continued-fraction representations (ICFR's) of the Laplace transform of C converges if, and only if, that of $K_N(t)$ does. In addition to yielding these rather formal results, (5) also facilitates the numerical calculation of TACF's.[7]

Our second main result is statement (VIII). That is, in order that the transport coefficient ($\sim D$) be positive and finite, we must require

$$\lim_{k\to\infty} \lambda_{k+1}/\lambda_k = 1 . \tag{53}$$

Unfortunately, (53) is not sufficient to prove that $0 < D < \infty$, as emphasized by an example given in Sec. V. Nonetheless, (53) can be of considerable value in analyzing the TACF semiempirically. For instance, suppose the first several even moments are known along with the transport coefficient. Then it may be possible to extrapolate the behavior of the λ's by means of a functional form consistent with the given data and (53). Such a procedure eliminates much of the arbitrariness inherent in many modeling studies.

The fact that the analytic properties of the TACF and its memory function should be related is, of course, not a novel idea. Corngold,[18] for example, has shown that in certain circumstances the amplitudes of $C(t)$ and $K_1(t)$ are proportional in the limit of large t. Since $C(t)$ and $K_1(t)$ bear the same relationship to one another as do $K_n(t)$ and $K_{n+1}(t)$ for all n [see relation (5)], it follows that $K_n(t)$ has the same asymptotic ($t \to \infty$) amplitude as $C(t)$ for all n, provided that $C(t)$ satisfies Corngold's[18] criteria. This result again shows the usefulness of relation (5) in extending certain analytic results for one C/K_n pair to a whole heirarchy of pairs such as $C/K_{m>n}$ and $K_m/K_{n>m}$.

The notion that the λ's may have regular properties is not new and, indeed, has formed the basis of at least one previous study[19] of TACF's rooted in continued-fraction theory. The general results we have pointed out seem not to have been previously obtained explicitly. Indeed, it has been suggested[3] that the behavior of the lowering coefficients may be hopelessly complex. This view, however, seems to be supported neither by known specific cases,[8] nor by the more general results reached here. The positivity of transport coefficients would seem to preclude purely random (positive) λ's, for example.

The relevance of our results to practical calculations of TACF's requires some knowledge of the lowering coefficients (or moments). Such information is available for harmonic solids[20] and, *via* molecular dynamics, is becoming increasingly more accessible for dense fluids.[7,21] Given a limited number of λ_j's, we may be able to extrapolate (as a function of j) their behavior to find the "order of infinity." For all but the simplest systems, it is certain to be simpler to estimate the order of infinity than actually to obtain the λ's.

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