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Time-correlation functions and spectral densities from modified moments*

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Modified moments provide coefficients in expansions for time-autocorrelation functions (TAF's) and for their spectral densities. The expansions for TAF's are very generally convergent; the expansions for their spectral densities converge when these densities satisfy sufficient continuity or smoothness conditions. Whenever a partial sum to the density is nonnegative, the corresponding partial sum to the TAF necessarily lies between the rigorous bounds recently obtained by Platz and Gordon. The accuracy of these expansions is illustrated by an application to the harmonic solid model considered by Platz and Gordon. The expansion for the TAF is consistently one or two orders of magnitude more accurate than the bounds obtained from the same number of moments and accurately represents the TAF to substantially longer times than do the bounds.

Recently Platz and Gordon[1] have shown how to obtain rigorous bounds for the real part of the *time-autocorrelation function* (TAF), $C(t)$, of a dynamical quantity Q:

$$C(t) \equiv \langle Q(t)Q(0)\rangle , \tag{1}$$

from initial time derivatives of the real part of the TAF. These time derivatives are simply related to even power moments μ_{2k} of a spectral density $I(\omega)$ which in many cases can be shown to be non-negative:

$$\mathrm{Re}\{C(t)\} = \int_{-\infty}^{\infty} \cos(\omega t) I(\omega)\, d\omega , \tag{2}$$

$$\frac{d^{2k}}{dt^{2k}} \mathrm{Re}\{ C(t)\} \big|_{t=0} = (-1)^k \mu_{2k} , \tag{3}$$

$$\mu_{2k} = \int_{-\infty}^{\infty} \omega^{2k} I(\omega)\, d\omega \quad \text{(see Ref. 2)}. \tag{4}$$

Such correlation functions arise in a wide variety of problems in physics and chemistry, including the behavior of solids,[3] liquids,[4] and magnetic systems.[5] Hence, it is of considerable interest to be able to make efficient use of information about the spectral density in the evaluation of these correlation functions.

Platz and Gordon's bounds for the TAF are obtained by replacing the true spectral density by a point spectrum which reproduces the known moments correctly. These bounds are thus the best possible if only the moments are known.

It is often the case that the spectral density is known, from general considerations, to obey certain continuity or smoothness conditions, even though its detailed form is unknown. For example, it may be known to be bounded, of bounded variation, continuous or even differentiable. It also frequently happens that the spectrum is known to be nonzero only on a finite interval, or that its asymptotic behavior is known for large values of its argument. In these cases it is natural to try to find approximations to the spectral density and its correlation function which reflect this additional information as well as that contained in the known moments.

In this paper we observe that appropriately chosen *modified moments* of the spectral density provide a natural and useful way of doing this, and that the approximate TAF's obtained by this method may be substantially more accurate than the bounds, and provide useful information about the true TAF to substantially longer times than the bounds, when the spectral density is well behaved. Modified moments[6–10] of the spectral density possess distinct advantages over the power moments. They can always be calculated from power moments when these are available,[9] and can sometimes be obtained more easily than the power moments by direct computation.[8] They stably determine quadrature formulas[6,7,9] (used in the bounding procedure) whereas the determination of quadrature formulas from the power moments is known to be exponentially ill conditioned.[7] This is particularly important for correlation functions, as the time out to which the bounds accurately determine the TAF is roughly proportional to the number of moments which can be used.[11] In addition, modified moments are coefficients in convergent expansions for TAF's and for their spectral densities when these densities are sufficiently well behaved. We show this below, and illustrate it by an application to the harmonic solid model considered by Platz and Gordon.

Because the cosine Fourier transform is sensitive only to the even part of $I(\omega)$, it will be convenient to use the alternative representation:

$$F(t)=\int_0^\infty G(x)\cos(x^{1/2}\tau)\,dx\,, \tag{5}$$

where

$$F(t)=\frac{\mathrm{Re}\{C(t)\}}{\mathrm{Re}\{C(0)\}}\,,$$

$$x=(\omega/\omega_m)^2,\quad \tau=\omega_m t\,, \tag{6}$$

$$G(x)\,dx=\frac{[I(\omega)+I(-\omega)]\,d\omega}{\int_{-\infty}^{\infty}I(\omega)\,d\omega}\,,$$

and where ω_m is any convenient constant which sets the scale on which $G(x)$ varies. In the case where $G(x)$ is nonzero only on a finite interval, ω_m will be taken to be the maximum frequency.

Let $H(x)$ be a non-negative density defined on the same interval as the unknown density $G(x)$ and having orthonormal polynomials $p_n^*(x)$,[12]

$$\langle p_l^* p_k^*\rangle_H=\int_0^\infty H(x)p_l^*(x)p_k^*(x)\,dx=\delta_{kl}\,. \tag{7}$$

The averages of these polynomials over $G(x)$ are *modified moments*:

$$\nu_n^*\equiv\langle p_n^*\rangle_G=\int_0^\infty G(x)p_n^*(x)\,dx\,. \tag{8}$$

The spectral density can be formally represented by an expansion in these orthonormal polynomials with coefficients which are just the modified moments:

$$G(x)\sim H(x)\sum_{n=0}^{\infty}\nu_n^* p_n^*(x)\,. \tag{9}$$

The convergence of such an expansion generally depends upon the nature of H and the smoothness properties of G, but can be established for a wide variety of problems of interest. It is desirable that $H(x)$ be nonzero on the same interval as $G(x)$ and be as similar to $G(x)$ as possible, particularly at the ends of the interval. This not only aids convergence, but makes it likely that the partial sums to Eq. (9) will themselves be non-negative densities, a point of importance below.

Equation (9) may be integrated term by term to obtain a formal expansion for the TAF:

$$F(t)\sim\sum_{n=0}^{\infty}\nu_n^* f_n(\tau)\,,\qquad f_n(\tau)=\int_0^\infty H(x)p_n^*(x)\cos(x^{1/2}\tau)\,dx\,. \tag{10}$$

This series can be shown[13] to converge to $F(t)$ under much more general conditions than those required for the convergence of Eq. (9), and can often be shown, as in the example considered below, to converge for any non-negative $G(x)$. When G and H are restricted to the unit interval, $f_n(\tau)$ can generally be shown, at any fixed τ, to vanish at least as rapidly as $[(\frac{1}{2}\tau)^{2n}/(2n)!]$, while ν_n^* can typically be bounded by $|\nu_n^*|\leq Bn^q$ with B and q positive and independent of n. When $G(x)$ satisfies boundedness, continuity or differentiability conditions, the ν_n^* can often be bounded by a *negative* power of n. In these cases, the series expansion (10) for $F(t)$ may be expected to converge substantially more rapidly than do the more general bounds.

The partial sums,

$$G_n(x)=H(x)\sum_{k=0}^{n}\nu_k^* p_k^*(x)\,, \tag{11}$$

provide a sequence of approximations to the spectral density which give the first $n+1$ moments correctly. If $G_n(x)$ is non-negative on the interval of definition of G, then the nth partial sum to $F(t)$ *will necessarily lie between the rigorous bounds* obtained from $n+1$ moments for all time t.

We illustrate this approach by an application to the cubic-close-packed (ccp) harmonic solid model used as an example by Platz and Gordon. For this system, the spectrum is known to be nonzero only on a finite interval so we may take $0\leq x\leq 1$. For harmonic solids in three dimensions, a particularly suitable choice for $H(x)$ is[8,9] $H(x)=(8/\pi)\times[x(1-x)]^{1/2}$ with (monic) orthogonal polynomials p_n satisfying the recursion relation,

$$p_{n+1}(x)=(x-\tfrac{1}{2})p_n(x)-\tfrac{1}{16}p_{n-1}(x)\,. \tag{12}$$

These are shifted Chebyshev polynomials of the second kind. The normalized polynomials $p_n^*(x)=(-4)^n p_n(x)$ can be reexpressed in the form:

$$p_n^*(x)=\frac{\sin(n+1)\theta}{\sin\theta}\quad(\sin^2\tfrac{1}{2}\theta=x)\,. \tag{13}$$

Under this transformation the orthogonal polynomial expansion for G becomes a Fourier series:

$$G(\sin^2\tfrac{1}{2}\theta)=\frac{4}{\pi}\sum_{n=0}^{\infty}\nu_n^*\sin(n+1)\theta\quad(0\leq\theta\leq\pi)\,. \tag{14}$$

Typical harmonic solid models in three dimensions satisfy sufficient boundedness and continuity conditions[3] that convergence of the Fourier series can be established.

For the nearest-neighbor ccp solid model, 40 exact modified moments have been obtained by direct computation.[8] In Fig. 1 we show the approximate spectral density obtained from these 40 modified moments. It is non-negative and accurately depicts the general features of the spectrum.

The Fourier series may be integrated term by term to obtain a convergent expansion in Bessel functions for $F(t)$:

$$F(t)=\sum_{n=0}^{\infty} \nu_n^*[J_{2n}(\tau)-J_{2n+4}(\tau)]. \qquad (15)$$

This series converges to $F(t)$ for *any* normalized non-negative $G(x)$ on $[0,1]$, even a point spectrum. The asymptotic behavior of $J_{2n}(\tau)$ for large n at any fixed τ is $J_{2n}(\tau)\sim(4\pi n)^{-1/2}(e\tau/4n)^{2n}$, while Eq. (13) shows that ν_n^* is bounded in magnitude by $(n+1)$ for any non-negative weight function. Thus the Bessel-function expansion converges to $F(t)$ extremely rapidly at any fixed τ once $n>\frac{1}{4}e\tau$. For typical model solids the bound on ν_n^* can be considerably strengthened. For example, if $G(x)$ possesses only the required Van Hove[14] singularities, the $|\nu_n^*|$ will decrease as $n^{-3/2}$. Since the maximum value of $J_{2n}(\tau)-J_{2n+4}(\tau)$ $(\tau\geq 0)$ is itself a decreasing function of n, it is to be expected that the partial sums remain reliable out to times larger than $4n/e$.

Using a method[11] similar to that of Ref. 1 we have verified that the partial sums $F_n(t)$ to Eq. (15) do indeed lie between the bounds obtained from the same number of moments. In addition, they approximate the TAF much more accurately than do the bounds obtained from the same number of moments. The error made by the partial sum is consistently one or two orders of magnitude less than the difference between the rigorous bounds. Furthermore, the partial sums give an accurate picture of the TAF out to a time equal to about three times the number of moments used, whereas the rigorous bounds separate and become of little value in determining the TAF at times slightly less than twice the number of moments used. The difference between successive partial sums provides a fairly reliable measure of the accuracy with which $F_n(t)$ approximates $F(t)$.

In Fig. 2 we see the approximate classical momentum TAF for the harmonic solid model obtained from 30 modified moments *superimposed* upon the approximate TAF obtained from 40 modified moments. The two curves are indistinguishable on the scale shown for τ less than 90, and they remain in phase for the entire range of the graph. The partial sums using 10 and 20 modified moments are essentially identical to this curve out to $\tau=30$ and 60, respectively, after which they drift out of phase with the exact curve and decay more rapidly with increasing time. The dashed curves indicate where the *rigorous bounds* from 20, 30, and 40 moments separate. Note that the interesting "ringing back" of the TAF at $\tau\approx 75$ is clearly shown by the Bessel-function expansion with only 30 terms, whereas it cannot be seen from the bounds, even with 40 moments. This ringing of the TAF is a general feature of spectral densities with Van Hove singularities.[11]

In summary, when the spectral density is known to be continuous or to satisfy some smoothness criterion, modified moments can be used to obtain approximate spectral densities and convergent expansions to time-autocorrelation functions which determine the TAF's more accurately and to longer times than do rigorous bounds from moments alone. The rigorous bounds have the advantage that, where they do determine the TAF precisely, there can be no question about the error involved.

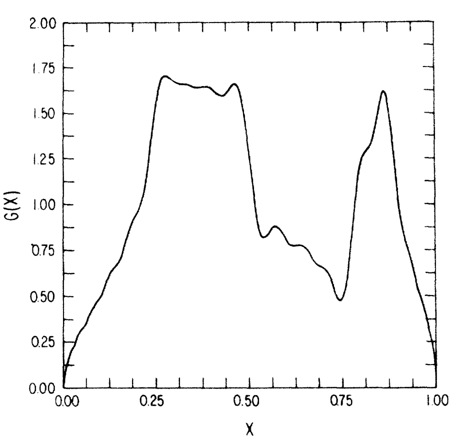

FIG. 1. Approximate spectral density for model harmonic solid from 40 modified moments. The density is positive, possesses the correct first 40 moments, and reproduces the qualitative features of the true spectrum with reasonable accuracy.

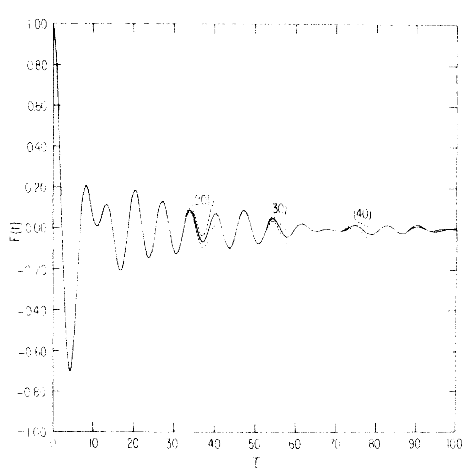

FIG. 2. Time-autocorrelation function for the model harmonic solid. The solid line is the superposition of the Bessel-function-series approximations from 30 and 40 modified moments. The pairs of dashed lines indicate where the rigorous bounds using 20, 30, and 40 modified moments separate.

It seems likely that these methods will often be complementary, the bounds being used to test the expansion which can then be reliably used to extend the results in time and precision.

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[2]Our Eqs. (1)–(4) are identical with those of Ref. 1 except for the correction of a typographical error in Eq. (4) of Ref. 1.

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[12]The asterisk is used to distinguish the *normalized* polynomials $p_n^*(x)$ and their modified moments ν_n^* from the *monic* polynomials $p_n(x)$ and their moments ν_n which were used in Refs. 8–10. All quantities are real.

[13]The proofs will be discussed in more detail elsewhere. They make use of theorems on the error of best polynomial approximation and of the asymptotic properties of the orthogonal polynomials. See, for example, G. Meinardus, *Approximation of Functions: Theory and Numerical Methods* (Springer, Berlin, 1967); and G. Szego, *Orthogonal Polynomials* (American Mathematical Society, Washington, D.C., 1959).

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