

fairly good fit for 0.1 M is obtained. A comparable fit occurs with $\alpha = -3$ and $\delta = 5.2 \times 10^{-3}$, implying $D \cong 4.96 \text{ \AA}$. Again with $\alpha = -3$, the 0.01 M MC results are very well fitted with $\delta = 0.0016$, implying $D \cong 7.25 \text{ \AA}$. Since mean field theory suggests that α should be concentration independent, it is reassuring that good fits are possible here for 1 to 0.01 M with a constant α value. It is likely that the LLGM requires an increasing lattice step size with decreasing concentration because a fluid situation is being approximated by a lattice model. Finally, dielectric saturation can be readily added to the LLGM,¹⁴ leading to a more realistic treatment. When MC results for both fluids and lattice situations become available it will be of interest to see how the LLGM α (and perhaps N as well) depends on d , ϵ_B , and M . The LLGM could then be of direct value to practicing electrochemists for both liquid and solid electrochemical applications since it would yield a much more accurate representation of DDL behavior than does conventional Gouy-Chapman theory.

¹⁴Work supported by National Science Foundation Grant DMR80-05236.

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Classical time-correlation functions and the Lanczos algorithm^{a)}

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(Received 19 May 1981; accepted 10 June 1981)

In recent years there has been a growing interest in the Lanczos algorithm¹ and its applications to problems in physics and chemical physics.² In particular, this algorithm was shown to be very useful in the calculation of correlation functions for slow motional ESR spectra.³ Generally, in past work the computational value of this algorithm was emphasized. The Lanczos algorithm is not widely recognized as a theoretical method that can concisely extract the relevant information from a general description of physical systems.⁴

The value of the Lanczos algorithm to theoretical analyses derives from its close relation to the more general method of moments,⁵ which may then be used in the study of the dynamics of classical statistical systems. One generally employs correlation functions to describe both the dynamical properties of a many particle system and the experimental data. We show here that the Lanczos algorithm leads in a natural way to their continued fraction representation.

Let us recall briefly the Lanczos algorithm. For a given self-adjoint operator A , defined in a Hilbert space ϵ and given a normalized starting vector $|z\rangle \in \epsilon$, the

method of moments⁵ defines the n th approximation A_n of A by the relation

$$A_n = P_n A P_n, \quad (1)$$

where P_n is the operator that projects any vector belonging to ϵ , onto the subspace ϵ_n constructed with the vectors $|z_{k+1}\rangle = A^k |z\rangle$ for $k=0$ to $n-1$. If, by means of a Schmidt orthonormalization procedure, we produce an orthonormal basis set spanning ϵ_n represented by the vectors $|k\rangle$ for $k=1$ to n , we obtain the recursion relation characteristic of the Lanczos algorithm^{1,3(b)}

$$\beta_k |k\rangle = (A - \alpha_{k-1}) |k-1\rangle - \beta_{k-1}^* |k-2\rangle. \quad (2)$$

A tridiagonal self-adjoint matrix T_n , with the α_k 's as diagonal elements ($\alpha_k \equiv \langle k | A_n | k \rangle = \langle k | A | k \rangle$) and the β_k 's as off-diagonal elements ($\beta_k \equiv \langle k | A_n | k-1 \rangle = \langle k | A | k-1 \rangle$), constitutes the representation of A_n in this new basis set.

The application of the Lanczos algorithm to the calculation of the classical autocorrelation function (acf) is straightforward, once the acf is written as

$$F(t) \equiv \overline{f(t)^* f(0)} = \langle P_{\epsilon_n}^{1/2} f | e^{-iLt} | P_{\epsilon_n}^{1/2} f \rangle, \quad (3)$$

where f is a function of the coordinates q and the momenta p of the system, the scalar product is defined as an integral over the phase space (i.e., $\langle \cdot \rangle = \int dp dq$), P_{eq} is the equilibrium distribution function ($P_{eq} = e^{-H/kT}/Z$) characterized by the Hamiltonian H , Z is the partition function $Z = \langle e^{-H/kT} \rangle$, and $L = L(p, q)$ is the classical Liouville operator which is Hermitian in the Hilbert space of the dynamical variables.⁶ Also we define $f(t)$ so that $\langle f(0) \rangle = \overline{f(0)} = 0$.

The following equation is obtained for the spectral function associated with $F(t)$:

$$\begin{aligned} \tilde{F}(\omega) &\equiv \lim_{\tau \rightarrow 0} \int_0^{\infty} \exp[-(i\omega + \tau)t] F(t) dt \\ &= \lim_{\tau \rightarrow 0} |f|^2 \langle 1 | [(i\omega + \tau)1 + i\mathbf{T}]^{-1} | 1 \rangle, \end{aligned} \quad (4)$$

where \mathbf{T} is the infinite self-adjoint tridiagonal (or continuant⁷) matrix generated by the Lanczos algorithm applied to L with the normalized $|z\rangle = |1\rangle \equiv (|f|^2)^{-1/2} \times |P_{eq}^{1/2} f\rangle$ as the starting vector [cf. Ref. 3(b) Appendix A for the simple details leading to the second equality]. We note that if the function f has a definite parity with respect to time reversal, then all the diagonal coefficients of \mathbf{T} are zero, since $L \rightarrow -L$ under time reversal. This is usually the case since most spectroscopic data are interpreted with acf's that are functions of molecular position and/or orientation. By means of standard techniques^{3(b), 7} the continued fraction⁷ representation of $\tilde{F}(\omega)$ is obtained from the continuant matrix of Eq. (4) as follows:

$$\begin{aligned} \tilde{F}(\omega) &= \lim_{\tau \rightarrow 0} |f|^2 \left\{ \frac{1}{(i\omega + \tau + i\alpha_1) + \frac{|\beta_2|^2}{(i\omega + \tau + i\alpha_2) + \dots}} \right. \\ &\quad \left. \dots \frac{|\beta_n|^2}{(i\omega + \tau + i\alpha_n) + \dots} \right\}. \end{aligned} \quad (5)$$

Equation (5) is, in fact, equivalent to the well-known Mori continued-fraction representation of the acf.^{8, 9} Moreover the memory function hierarchy is easily recovered once the generalized memory function¹⁰ $K_j(t)$ is defined as

$$K_j(t) \equiv |\beta_j|^2 \langle j | \exp[-i(1 - P_{j-1})L t] | j \rangle \quad (6)$$

(see appendix below).

Thus we see that:

(1) The application of the Lanczos algorithm to classical statistical systems constitutes a simple method for obtaining the continued fraction representation of the correlation function and its memory function hierarchy.¹¹ This suggests its possible utility as an approach that could complement the well-known memory function methods.^{10, 12, 13} Such studies would be aided by the established connection between the Lanczos algorithm and the method of moments,⁵ continued fractions,⁷ and Padé determinants.¹⁴

(2) In the context of the Lanczos algorithm one can develop useful approaches in approximating Eq. (5). For example, in numerical analysis¹ the Lanczos algorithm is employed with the finite dimensional approxi-

mation \mathbf{A}_n of the operator \mathbf{A} . This would be equivalent to a truncation of the infinite tridiagonal matrix \mathbf{T} in Eq. (4) by assuming that β_n is zero. However, in the usual memory function approach, when one considers a $K_n(t)$ that is rapidly decaying compared to $F(t)$ [e.g., $K_n(t) \approx K_n(0) \delta(t)/\gamma$, where γ plays the role of a decay rate], then a truncated form of \mathbf{T} is still generated, but correspondingly an imaginary contribution $[-iK_n(0)/\gamma]$ would be introduced to the diagonal element α_{n-1} (see appendix below), thus destroying the self-adjoint nature of \mathbf{T} and leading to irreversible behavior. It would also be of interest to relate such formal approximations to the application of the Lanczos algorithm in calculating an acf from a stochastic model represented by a Fokker-Planck equation, as previously discussed.^{3(b)} We note that the Lanczos algorithm has indeed been recently extended to non-self-adjoint complex matrices \mathbf{A} , which are generated in the analysis of such Fokker-Planck equations.^{3(b)}

(3) There is considerable current interest in the use of variations of Mori-type memory functions, projection operators, and continued fractions in the modeling of microscopic molecular dynamics in condensed phases.¹⁵ The computational efficiency of the Lanczos algorithm^{2, 3(b)} strongly suggests the possibility of its practical use for computer calculations in this general area of microscopic molecular dynamics. For this purpose, a matrix representation of the approximate or model Liouville operator is needed. It would also be of interest to explore the relationship between such an approach based on the Lanczos algorithm to the approaches currently being used¹⁵ given what we have already noted in paragraph (1) above.

Appendix: Starting with Eq. (6) as the definition of the j th memory function, we apply the Lanczos algorithm [i.e., [i.e., Eq. (2)] to $L_j \equiv (1 - P_{j-1})L$, with $|j\rangle$ as the starting vector. This procedure generates the vectors $|j+1\rangle$, $|j+2\rangle$, $|j+3\rangle$, ... and the infinite tridiagonal matrix $\mathbf{T}_j = (1 - P_{j-1})\mathbf{T}(1 - P_{j-1})$. Then, by analogy with Eqs. (3)-(5), we obtain

$$\begin{aligned} \tilde{K}_j(\omega) &= \lim_{\tau \rightarrow 0} |\beta_j|^2 \langle j | [(i\omega + \tau)1 + i\mathbf{T}_j]^{-1} | j \rangle, \\ &= \lim_{\tau \rightarrow 0} |\beta_j|^2 \\ &\quad \times \left\{ \frac{1}{i\omega + \tau + i\alpha_j + |\beta_{j+1}|^2 \langle j+1 | [(i\omega + \tau)1 + i\mathbf{T}_{j+1}]^{-1} | j+1 \rangle} \right\}, \\ &= \frac{K_j(0)}{i\omega + i\alpha_j + \tilde{K}_{j+1}(\omega)}, \end{aligned} \quad (7)$$

which is easily related to Eq. (5). [Note $K_j(0) = |\beta_j|^2$]. Inversion of Eq. (7) yields the time domain result

$$\frac{d}{dt} K_j(t) = -i\alpha_j K_j(t) - \int_0^t K_{j+1}(t-s) K_j(s) ds, \quad (8)$$

which is the characteristic equation for the memory functions.⁸

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COMMENTS

The MPB and BBGY potential theories for a 2:2 restricted primitive model electrolyte at low concentrations

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(Received 13 August 1980; accepted 2 September 1980)

Monte Carlo calculations for a 2:2 restricted primitive model electrolyte have recently been presented by Valleau and Cohen,¹ and Valleau, Cohen, and Card.² Valleau, Cohen, and Card have further used the MC data to make a careful appraisal of the structural and thermodynamic properties predicted by the various electrolyte theories. They find that the HNC, BGY,³ MPB, and ORPA + B₂ theories⁴ are the most successful. Here we wish to supplement previous MPB results⁵ (for the MPB3 equation) at the lower concentrations to complete comparisons with the new MC data. For $c \leq 5 \times 10^{-4}$ M the simpler MPB1 equation was used as the MPB1 and MPB3 results are indistinguishable at these very low concentrations. The reduced configurational energy U/NkT and the virial osmotic coefficient ϕ_v are given in the table while the deviation of U/NkT from the Debye-Hückel limiting law is given in the figure. The figure supports Valleau, Cohen, and Card's statement that the MPB theory is likely to provide an excellent approxima-

tion at low concentrations. This result is not surprising, as this theory is closely related to the Debye-Hückel

TABLE I. Reduced configurational energy U/NkT and the virial osmotic coefficient ϕ_v for the MPB3 (Ref. 5) and BBGY3 (Ref. 7) theories. The 2:2 electrolyte parameters are those used by Valleau, Cohen, and Card (Ref. 2).

\sqrt{c}	$-U/NkT$		ϕ_v	
	MPB	BBGY	MPB	BBGY
0.01	0.128		0.964	
0.025	0.361	0.362	0.908	0.908
0.05	0.692	0.704	0.835	0.831
0.075	0.947	0.970	0.781	0.773
0.1	1.149	1.184	0.741	0.728
0.15	1.458	1.514	0.683	0.663
0.2	1.690	1.767	0.643	0.619