Can the Velocity Autocorrelation Function Decay Exponentially?

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For Hermitian many-body systems, admissible functions for the velocity autocorrelation function form a certain invariant of time. This property originates from a basic recurrence relation. The exponentially decaying function cannot form an invariant and therefore cannot be admissible.

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The velocity autocorrelation function (VAF) is a key quantity in nonequilibrium statistical mechanics, from which basic transport properties can be calculated.[1] The VAF is defined as $\mathcal{V}(t) = (v(t), v(0))$, where $v(t)$ denotes the velocity of a particle at time t in a homogeneous fluid at some fixed temperature and the inner product means the Kubo scalar product. In the high-temperature or classical limit, the inner product may be replaced by $\langle v(t)v(0)\rangle$ where the angular brackets denote an appropriate ensemble average. The self-diffusion constant D is obtained from the VAF by the following well-known relation in some suitable units,

$$D = \int_0^\infty dt\, \mathcal{V}(t).$$

Given a microscopic model, one can in principle obtain the velocity time evolution $v(t)$, and hence $\mathcal{V}(t)$ and D, by solving the Heisenberg equation of motion or the *generalized* Langevin equation.[2] To do so is a very difficult task. Rarely does one in fact know the VAF from first principles. In practice one usually assumes that it has an exponential form $\mathcal{V}(t) \sim \exp(-\gamma t)$, where γ is a nonnegative constant, e.g., the friction coefficient.[3] The exponentially decaying form yields the famous Einstein relation $D\gamma = \text{const}$ for a fixed temperature. The recovery of the Einstein relation appears to provide an added measure of sanction for the use of this form for the VAF.

For $t \to 0$ the exponential form does not meet the well recognized condition $d\mathcal{V}(0)/dt = 0$. That is, the VAF must have zero initial slope.[4] For $t \to \infty$ the exponential form does not appear to violate any known conditions. Hence, it is generally believed that, for long times, the exponential form is still valid or appropriate.[5-7] Its Fourier transform (the Lorentzian), for example, is widely used in semiphenomenological spectral studies of fluids, magnets, and other systems. In dynamical critical phenomena the notion of slowing down is intimately linked to the Lorentzian shape of the scattering function.[8-10] It is for this reason that long-time tails in the VAF [i.e., $\mathcal{V}(t) \sim t^{-k}$, $0 < k < \infty$ and $t \to \infty$] first observed in computer experiments came as such a surprise.[11]

It is possible to test whether the VAF can be exponentially decaying at any time. Let H denote the Hamiltonian of our system, which may be a fluid or magnet. H is assumed to be Hermitian. Let A be a dynamical variable at $t = 0$, also Hermitian, which may be the velocity of a particle (tagged or untagged) or the total spin at some fixed wave vector. The time evolution of A is given by $A(t) = (\exp iLt)A$, where $LA = [H, A]$. Recently I showed that $A(t)$ has solutions in the form[2]

$$A(t) = \sum_{\nu=0}^{\infty} a_\nu(t) f_\nu, \qquad (1)$$

where $\{f_\nu\}$ is a set of orthogonalized basis vectors which span the Hilbert space of A, denoted by $\mathcal{S}$. In this space, $\{a_\nu\}$ is a set of real, linearly independent functions of time. These functions satisfy the *initial* condition $a_0(0) = 1$ and $a_\nu(0) = 0$ if $\nu \geq 1$. They are related by the following recurrence relation (RR):

$$\Delta_{\nu+1} a_{\nu+1}(t) = -\dot{a}_\nu(t) + a_{\nu-1}(t), \quad \nu \geq 0, \qquad (2)$$

where $a_{-1} \equiv 0$, $\dot{a}_\nu = da_\nu/dt$, and $\Delta_\nu = (f_\nu, f_\nu)/(f_{\nu-1}, f_{\nu-1})$ with $\Delta_0 \equiv 1$. Observe that Δ_ν represents the relative norm or length of f_ν to $f_{\nu-1}$, which are a pair of adjacent basis vectors of the space $\mathcal{S}$. This entire set of lengths completely defines the geometry of the realized Hilbert space (e.g., dimensionality, shape). The lengths are model dependent. I shall term Δ_ν the νth *recurrant*. The general form of a_ν depends sensitively on the behavior of the recurrants as a function of ν. The recurants themselves (through their characteristic properties) are coupled to time explicitly. Also, an admissible set of functions for $\{a_\nu\}$ must realize a recurrence relation which is congruent to the above RR [Eq. (2)]. Hence if, for example, an admissible function for a_0 is known, a complete set of functions for $\{a_\nu\}$ can be found by the RR.

From the Hermitian property of L, we must have $(A(t), A(t))/(A, A) = 1$ for any t. Hence, it follows that

$$\sum_{\nu=0}^{\infty} [a_\nu(t)]^2 \prod_{\mu=1}^{\nu} \Delta_\mu = 1. \qquad (3)$$

That is, the length of the vector $A(t)$ in $\mathcal{S}$ is an invariant of time.[2] This property is useful for testing whether a particular set of functions is an admissible set. Let $\tilde{a}_0$ be a trial function, forming a trial set $\{\tilde{a}_\nu\}$ via the RR. To be admissible, i.e., $\tilde{a}_\nu = a_\nu$ for every $\nu \geq 0$, the trial set must form the above invariant.

If A represents the velocity, then by definition $a_0(t)$ is the VAF. We can immediately test whether the exponential form for the VAF is admissible. Let $\tilde{a}_0(t) = \exp(-\gamma t)$. By the RR, we obtain $\tilde{a}_\nu(t) = u_\nu \exp(-\gamma t)$, for every $\nu \geq 1$, where u_ν is a coefficient, $u_0 = 1$, $u_1 = \gamma/\Delta_1$, $u_2 = (1 + \gamma^2/\Delta_1)/\Delta_2$, etc. These trial functions are *not* linearly independent and the recurrants are *not* coupled to time. Furthermore,

$$\tilde{A}(t) = \sum_{\nu=0} \tilde{a}_\nu(t) f_\nu = \Big(\sum_{\nu=0} u_\nu f_\nu\Big)\exp(-\gamma t). \qquad (4)$$

The trial functions cannot form an invariant. I therefore conclude that the exponential form cannot represent the VAF.[12]

We shall now obtain further implications of the exponential function. The time evolution of A can be regarded as caused by its *generalized* random force $\mathfrak{F}(t)$.[13] I have shown that[2]

$$\mathfrak{F}(t) = \sum_{\nu=1}^{\infty} b_\nu(t) f_\nu, \qquad (5)$$

where $\{b_\nu\}$ is a set of real, linearly independent functions of time. In particular, b_1 is the memory function which appears in the kernel of the generalized Langevin equation for $v(t)$.[14] These memory functions, referring to $\{b_\nu\}$ collectively, satisfy the initial condition $b_1(0) = 1$ and $b_\nu(0) = 0$ if $\nu \geq 2$. They also satisfy the RR [Eq. (2)] with $\nu \geq 1$ and $b_0 \equiv 0$, hence without the first recurrant. The generalized random force $\mathfrak{F}(t)$ belongs to a linear manifold of $\mathcal{S}$. In this subspace, the length of $\mathfrak{F}(t)$ is also an invariant of time.[2] I have further shown that[2]

$$b_\nu(z) = a_\nu(z)/a_0(z), \quad \nu \geq 1, \qquad (6)$$

where $a_\nu(z) = \;[a_\nu(t)]$, where is the Laplace transform operator. Our trial function $\tilde{a}_0(t) = \exp(-\gamma t)$ directly yields $\tilde{b}_1(t) = u_1 \delta(t)$. Hence, if the VAF is an exponential function, the memory functions must necessarily be delta functions. Also from (6), we have

$$a_\nu(t) = \int_0^t dt'\, b_\nu(t - t') a_0(t'), \quad \nu \geq 1. \qquad (7)$$

Hence if the memory functions are delta functions, the trial VAF functions $\{\tilde{a}_\nu\}$ cannot be linearly independent and their form cannot sensitively depend on the recurrants.

The initial condition for $\{a_\nu\}$ and the RR are sufficient to establish the boundary conditions at the origin (i.e., $t = 0$) for the VAF.[15] From $\Delta_1 a_1(t) = -\dot{a}_0(t)$, $\Delta_2 a_2(t) = -\dot{a}_1(t) + a_0(t)$, etc., we obtain $\dot{a}_0(0) = 0$, $\ddot{a}_0(0) = -\Delta_1 < 0$, $\dddot{a}_0(0) = 0$, $\ddddot{a}_0(0) = \Delta_1(\Delta_1 + \Delta_2) > 0$, etc. All odd derivatives vanish at the origin. These boundary conditions were originally obtained from linear response theory.[4] The short-time behavior of the VAF can also be established. Using the RR, I have shown that[2]

$$a_0(z) = \cfrac{1}{z + \cfrac{\Delta_1}{z + \cfrac{\Delta_2}{z + \cdots}}}. \qquad (8)$$

Hence $a_0(t)$ can be obtained by applying $\mathcal{T}^{-1}$,

$$a_0(t) = 1 - \Delta_1 t^2/2! + \Delta_1(\Delta_1 + \Delta_2)t^4/4! - \Delta_1[(\Delta_1 + \Delta_2)^2 + \Delta_2\Delta_3]t^6/6! + \Delta_1[(\Delta_1 + \Delta_2)^3 + \Delta_2\Delta_3(\Delta_1 + \Delta_2) + \Delta_2\Delta_3(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4)]t^8/8! \ldots. \qquad (9)$$

The coefficient of t^4 was first given by Nijboer and Rahman[16] in their work of slow neutron scattering in classical fluids.

The condition by which $\exp(-\gamma t)$ was excluded from the class of admissible functions for the VAF is the Hermiticity of our Hamiltonian H. To our Hamiltonian H of many-body interaction energies, we now add a coupled non-Hermitian term h (e.g., dissipative, coupled to the reservoir). If the dynamics of this enlarged system $H' = H + h$ is describable by an exponentially decaying function, then dynamically $H' \sim h$. For example, the friction coefficient γ is a property of h and not related to the recurrants of H. The VAF for non-Hermitian systems need *not* satisfy the boundary condition at the origin imposed by the Hermiticity of H. This explains why an exponentially decaying function, in spite of its inability to meet the boundary conditions at the origin, can still realize the Einstein relation.[17]

There have been a number of attempts to calculate the transport coefficients of apparently dissipative systems by using the recurrants of H.

A standard practice is to approximate the memory function by a three-pole function. This kind of approximation is equivalent to representing the VAF by an exponentially decaying function. Hence, the three-pole phenomenology may not be meaningful if one is attempting to relate the transport coefficients to the collective or many-body terms of H.[18-20]

Finally, the class of admissible functions for the VAF includes the Gaussian, the cylindrical and spherical Bessel functions, and some others related to them.[2] Some of these functions can be physically realized by certain Hermitian systems such as the spin van der Waals model,[21] the electron gas models,[12] and the linear chain of nearest-neighbor–coupled harmonic oscillators.[22,23]

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[1]Y. Pomeau and P. Resibois, Phys. Rep. 19C, 64 (1975).

[2]M. H. Lee, Phys. Rev. B 26, 2547 (1982).

[3]E.g., S. W. Lovesey, *Condensed Matter Physics: Dynamic Correlations* (Benjamin, Reading, Mass., 1980). The exponentially decaying function is a solution of the classical Langevin equation, which is a phenomenological equation of motion. See pp. 24–26.

[4]E.g., W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Oxford Univ. Press, London, 1970), pp. 384, 385.

[5]J. R. D. Copley and S. W. Lovesey, Rep. Prog. Phys. 38, 461 (1975). See p. 525.

[6]H. van Beijeren, Rev. Mod. Phys. 54, 195 (1982). See p. 197.

[7]See Ref. 1 (p. 67) and Ref. 3 (p. 40). Some even assert that the exponential form can be more or less proved by modern statistical physics. M. Steiner *et al.*, Adv. Phys. 25, 87 (1976); see p. 153.

[8]H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, London, 1971), pp. 200–214.

[9]P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, New York, 1967), pp. 212, 213.

[10]W. Marshall and R. D. Lowde, Rep. Prog. Phys. 31, 705 (1968).

[11]A number of theoretical papers on long-time tails and their origins have since appeared, nearly all employing hydrodynamic or similar approximations. See Ref. 1 for references. There are still no rigorous results which definitively indicate the existence or absence of long-time tails in the VAF. See P. Resibois and M. DeLeener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977), p. 360; and R. F. Fox, Physica (Utrecht) 118A, 383 (1983).

[12]If, as $t\to\infty$, $\tilde{a}_0(t)=t^{-k}\theta(t)$, where $0<k<\infty$ and $\theta(t)$ is a weak function of time, it can form a set of linearly independent functions. Hence the long-time tails are not excluded by my argument. For example, the relaxation functions due to density fluctuations in an electron gas are linearly independent. For the two-dimensional ideal and interacting electron gases, $k=\frac{1}{2}$ and $\frac{3}{2}$, respectively, and for the three-dimensional ideal electron gas, $k=1$. See M. H. Lee and J. Hong, Phys. Rev. Lett. 48, 634 (1982).

[13]The term random force usually carries the implications that the process is Gaussian and that it has a white power spectrum. To avoid such implications, I shall refer to the random force in the *generalized* Langevin equation as the generalized random force.

[14]See Ref. 3, pp. 56–64.

[15]This result is given to indicate the general validity and utility of the method of recurrence relations.

[16]B. R. A. Nijboer and A. Rahman, Physica (Utrecht) 32, 415 (1966). Also see Refs. 3–5.

[17]In the literature there seems to be a confusion over this seeming incompatibility. See Refs. 3 and 4.

[18]The three-pole phenomenology for the memory function was introduced by H. Mori [Prog. Theor. Phys. 34, 399 (1965)] and used by a number of people. See, e.g., S. W. Lovesey and R. A. Meserve, Phys. Rev. Lett. 28, 614 (1972); P. Fulde *et al.*, Phys. Rev. Lett. 35, 1776 (1975); G. Mukhopadyay and A. Sjölander, Phys. Rev. B 17, 3589 (1978); H. De Raedt and B. De Raedt, Phys. Rev. B 18, 2039 (1978); P. A. Lindgard, Phys. Rev. B 27, 2980 (1983).

[19]It is well known that spectral measurements of many systems show a Lorentzian line shape, which seems to imply that these systems are largely dissipative. Suppose that some systems are known to be nondissipative or only very slightly dissipative and still they yield a Lorentzian shape within some limits of the frequency. This can only be so if the admissible functions for them are good approximations to the exponential function in the range where the experimental measurements are reliable. One can test the validity of the above view with specific examples; e.g., by measuring the spectra for systems for which one knows the admissible functions exactly.

[20]The question of decay also arises when one is dealing with a system in contact with a heat bath, in which the effects of the heat bath are first averaged over. The subsystem dynamics then evolves in a complex fashion and it may decay. See A. K. Rajagopal, K. L. Ngai, R. W. Rendell, and S. Teitler, J. Stat. Phys. 30, 285 (1983); K. L. Ngai, A. K. Rajagopal, R. W. Rendell, and S. Teitler, Phys. Rev. B (to be published). Also see M. N. Hack, Phys. Lett. 88A, 228 (1982), and 90A, 220 (1982).

[21]R. Dekeyser and M. H. Lee, Phys. Rev. B 19, 265 (1979); R. Botet, R. Jullien, and P. Pfeuty, Phys. Rev.

Lett. 49, 478 (1982); R. K. Pathria, J. Math. Phys. 24, 1927 (1983).

[22]R. F. Fox, Phys. Rev. A 27, 3216 (1983). See especially Eq. (54).

[23]C. W. Ford, M. Kac, and P. Mazur [J. Math. Phys. 6, 504 (1965)] considered a system of coupled harmonic oscillators and obtained an exponentially decaying function for the VAF's under some special conditions. In this work, a tagged oscillator is in contact with a large number of other oscillators, which are collectively made to act as a heat bath for the tagged one. Because of averaging over the heat bath, the Hamiltonian does not remain Hermitian. Also they introduce a high-frequency cutoff. This cutoff enables them to transform the canonical equations of motion exactly into the form of the classical Langevin equation (CLE). It was noted in Ref. 3 that the exponential function is a solution of the CLE. If the VAF were an exponential function, its memory function must be a delta function [see the section containing Eqs. (5)–(7)]. Then the generalized Langevin equation reduces to the CLE. Hence, having this cutoff is equivalent to assuming the delta-function form for the memory function. The cutoff cannot be rigorously justified. These authors introduced it to circumvent an incipient divergence in their interaction integral and made no attempt to justify it mathematically. The VAF for a system of coupled harmonic oscillators can be obtained exactly if the coupling is limited to nearest neighbors (see Ref. 22). For this case the VAF is found to be the cylindrical Bessel function of order zero, an admissible function according to the present work.