ture and input-beam intensity. Experiments without the aperture and with beams with irregular transverse intensity distributions showed that the self-defocusing tends to smooth out the transverse intensity profile of the propagating beams. Self-defocusing always increased the beam divergence in our results. There was no evidence of absorption of light by the vapor, and at 124 °C for $\sigma^-$ light an upper limit for the absorption coefficient $\alpha$ is given by the low-level steady-state result $\alpha = 0.9 \times 10^{-3}$ cm$^{-1}$. When multimode dye-laser output was obtained, strong third-order mixing occurred in the rubidium vapor and indicated that the response time of the resonant electronic nonlinearity was much faster than 1 nsec, the period of the beat note between adjacent longitudinal modes of the dye laser.


## ACKNOWLEDGMENTS

The authors would like to acknowledge the invaluable assistance of R. J. Bennett in all phases of the experiment and the data reduction. Many useful discussions were held with Michael M. T. Loy. We also thank Professor W. Kaiser and Dr. M. Maier for information about their computation of self-focusing.


*Work of this author was partially supported by ONR under Contract No. N00014-70-C-0187.


[1]J. P. Gordon, E. C. C. Leite, R. S. Moore, S. P. S. Porto, and J. R. Whinnery, J. Appl. Phys. 36, 3 (1965).

[2]S. A. Akhmanov, D. P. Krindach, A. V. Migulin, A. P. Sukhorukov, and R. V. Khokhlov, IEEE J. Quantum Electron. QE-4, 568 (1968).

[3]F. W. Dabby, R. W. Boyko, C. V. Shank, and J. R. Whinnery, IEEE J. Quantum Electron. QE-5, 516 (1969).

[4]D. Grischkowsky, Phys. Rev. Letters 24, 866 (1970).

[5]A. Javan and P. L. Kelley, IEEE J. Quantum Electron. QE-2, 470 (1966).

[6]S. A. Akhmanov, A. I. Kovrigin, S. A. Maksimov, and V. E. Ogluzdin, Zh. Eksperim. i Teor. Fiz. Piz'ma v Redaktsiyu 15, 186 (1972) [Sov. Phys. JETP Letters 15, 129 (1972)].

[7]I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. 141, 391 (1966).

[8]A. V. Nurmikko and S. E. Schwarz, Appl. Phys. Letters 20, 346 (1972).

[9]I. I. Rabi, N. F. Ramsey, J. Schwinger, Rev. Mod. Phys. 26, 167 (1954).

[10]For temperatures below about 140 °C the homogeneous linewidth of the $^2P_{1/2}$ transition is not broadened by resonant collisions (Ref. 13) but is determined by the lifetime $\tau = 28$ nsec of the excited state. $T_1 = \tau$, and below 140 °C, $T_2 = 2T_1$. The dye-laser pulse width was 10 nsec, $\delta\nu/c < 0.005$ cm$^{-1}$, and $|\nu - \nu_0|/c = 0.45$ cm$^{-1}$; consequently, to a good approximation the conditions for adiabatic following were satisfied.

[11]The number density of rubidium atoms in the $M_J = \pm\frac{1}{2}$ Zeeman state of the $5\,^2S_{1/2}$ level is $N_e = \frac{1}{2}N = 1 \times 10^{13}/\text{cm}^3$ at 124 °C; $p_{12} = 6.16 \times 10^{-18}$ esu for the matrix element for the $\sigma^{\mp}$ transition between the $5\,^2S_{1/2}$, $M_J = \pm\frac{1}{2} \longleftrightarrow 5\,^2P_{1/2}$, $M_J = \mp\frac{1}{2}$ Zeeman states of the rubidium atom.

[12]P. L. Kelley, Phys. Rev. Letters 15, 1005 (1965).

[13]Ch'en Shang-Yi, Phys. Rev. 58, 884 (1940).

[14]R. E. Honig, RCA Rev. 18, 195 (1957).

[15]A. N. Nesmeyanov, *Vapor Pressure of the Elements* (Academic, New York, 1963).


PHYSICAL REVIEW A VOLUME 6, NUMBER 4 OCTOBER 1972

# Behavior of Autocorrelation Functions*


Noel Corngold

*Department of Engineering and Applied Science, California Institute of Technology, Pasadena, California* 91109


(Received 15 May 1972)

This paper is concerned with the behavior of the autocorrelation and memory functions of statistical mechanics as $t \to \infty$. A simple calculation shows that for a large class of models leading to power-law behavior, the two functions have opposite sign and common functional behavior in the limit $t \to \infty$.

## INTRODUCTION

The calculation of a typical autocorrelation function (acf) $\Phi(t)$ via an integrodifferential equation

$$\frac{d}{dt}\Phi(t) = -\int_0^t d\tau\, K(t-\tau)\Phi(\tau), \quad \Phi(0) = 1 \tag{1}$$

whose kernel is the appropriate "memory function (mf)," is of great utility in modern statistical mechanics.[1] However, little is known, in general, about the quantities $\Phi(t)$ and $K(t)$. It is the purpose of this paper to point out simple relations which must exist between these functions when the long-time behavior of the acf is of certain nonexponential varieties. These relations are summarized in Eqs. (13). Since there has been considerable in-

terest[2] in the power-law behavior of acf's, perhaps these results will prove valuable.

Our discussion makes use of $\tilde{\Phi}(s)$ and $\tilde{K}(s)$, the Laplace transform functions of the acf and the mf. The long-time behavior will be extracted from the behavior of these functions in the neighborhood of their dominant singularities. We begin by noting that Eq. (1) implies

$$\tilde{\Phi}(s) = 1/[s + \tilde{K}(s)] , \tag{2}$$

$$\tilde{K}(s) = 1/\Phi(s) - s . \tag{3}$$

Next, we list some of the assumptions necessary to secure our results:

(i) The acf and the mf are real integrable functions of $t$, $0 \leq t < \infty$.

(ii) The long-time behavior of the acf is "slower than exponential" (e.g., is power law). That is, $\Phi(t)e^{\epsilon t} \to \infty$ for all $\epsilon > 0$ as $t \to \infty$. The divergence may be oscillatory. Thus, $\tilde{\Phi}(s)$ and $\tilde{K}(s)$ are analytic in the half-plane $\sigma = \mathrm{Re}\, s > 0$. Neither may possess poles at points on the imaginary axis. $\tilde{\Phi}(s)$, which must be singular on the axis, may have isolated branch points there. Such points will be common to $\tilde{\Phi}(s)$ and $\tilde{K}(s)$. On the other hand, $\tilde{\Phi}(s)$ may also have essential singularities upon the axis. We also make the following assumption:

(iii) The only singularities of $\tilde{\Phi}(s)$, and, therefore, of $\tilde{K}(s)$, upon the imaginary axis are branch points. All other singularities $s_\nu$ in the left (cut) plane have $|s_\nu| \geq \epsilon_3 > 0$.

An example of the type of function that is acceptable is as follows: Let $\Phi(t)$ have an asymptotic expansion, as $t \to \infty$, such that the error after $n$ terms is *exponentially* small. (The individual "terms" may consist of sums of powers, multiplied by exponentials; see Doetsch.[3]) Then, the sole singularities on the imaginary axis are branch points.
It is not easy to find an example of a $\Phi(t)$ satisfying (1) and (2) but leading to a $\tilde{\Phi}(s)$ whose dominant singularity is an essential singularity. Thus,

$$\Phi(t) = J_0(2t^{1/2}) \sim \frac{1}{\pi^{1/2}} \frac{\cos(2t^{1/2} - \frac{1}{4}\pi)}{t^{1/4}}$$

would seem "physical" enough, and leads to $\tilde{\Phi}(s) = (1/s)e^{-1/s}$. The $\tilde{K}(s)$ which follows also has an essential singularity at $s = 0$. However, its inverse transform $K(t)$ is $\sim [1/(4\pi)^{1/2}] \exp(2t^{1/2})/t^{5/4}$ and is not acceptable.

## ANALYSIS

We begin with the simplest case, when the asymptotic behavior is described by a single branch point at $s = 0$. A simple example is provided by the transform pair

$$\Phi_0(t) = \sum_{m=0}^{N} a_m t^{-\gamma_n} + O(e^{-\epsilon t}) , \quad \epsilon > 0 \tag{4}$$

$$\tilde{\Phi}_0(s) = \sum_{m=0}^{N} a_m \Gamma(1 - \gamma_m) s^{\gamma_m - 1} + g(s) , \tag{5}$$

where $g(s)$ is analytic in a neighborhood of the origin. If some

$$\gamma_m = p \quad (p = 1, 2, \ldots)$$

the corresponding term in Eq. (5) is to be replaced by

$$a_m[(-)^p/(p-1)!]s^{p-1} \ln s .$$

If the $\gamma_m$ (and $a_m$) are complex they occur in pairs. We shall not make use of a specific form of $\tilde{\Phi}(s)$ in the following.

By hypothesis, the transform $\tilde{\Phi}(s)$, originally defined in a right half-plane may be continued into a (cut) half-plane $\mathrm{Re}\, s > \epsilon_1 < 0$. The asymptotic behavior in $t$ is determined by the behavior of $\tilde{\Phi}(s)$ in the neighborhood of the branch point. We shall distinguish the case A in which $\tilde{\Phi}(s)$ approaches a unique, finite limit as $s \to 0$ along any ray in the cut plane. [If $\tilde{\Phi}(0)$ is zero and $\tilde{\Phi}(s) = O(s)$, special difficulties arise. This unusual case will be denoted $A_0$.] Case A is somewhat of a generalization of the requirement that $\tilde{\Phi}(0)$ exist as $s \to 0$ along the positive real axis, i.e., that the "diffusion coefficient" exists. To illustrate via our simple example, Eq. (5), let the $\gamma_m$ be ordered so that $\mathrm{Re}\,\gamma_0 \leq \mathrm{Re}\,\gamma_1 \leq \cdots$. Then, if $\mathrm{Re}\,\gamma_0 \geq 1$, the case A behavior holds. If $1 > \mathrm{Re}\,\gamma_0 > 0$, the acf approaches zero, but $\tilde{\Phi}(0)$ does not exist. We call this case B.

Since $\tilde{\Phi}(s)$ is real for real $s$, the continuation produces a function which assumes boundary values:

$$\tilde{\Phi}(\eta e^{\pm i\pi}) = \tilde{\Phi}_0(\eta) \pm i\tilde{\Phi}_1(\eta) \tag{6}$$

on the edges of the branch cut. In case A we must have $\tilde{\Phi}_1(\eta) \to 0$ as $\eta \to 0$. Now we deform the inversion contour around the singularity and along a portion of the cut. The contribution from the portion encircling the branch point vanishes (in cases A, $A_0$, and B) and a simple calculation gives

$$\Phi(t) \to -(1/\pi)\int_0^{\epsilon_2} d\eta\, \tilde{\Phi}_1(\eta) e^{-\eta t}, \tag{7}$$

with $\epsilon_2 < |\epsilon_1|$, $t \to \infty$. In cases A and B, a similar treatment gives

$$K(t) \to -(1/\pi)\int_0^{\epsilon_2} d\eta\, \tilde{K}_1(\eta) e^{-\eta t} , \tag{8}$$

with

$$\tilde{K}(\eta e^{\pm i\pi}) = \tilde{K}_0(\eta) \pm i\tilde{K}_1(\eta) \tag{9}$$

$$= \frac{1}{\tilde{\Phi}(\eta e^{\pm i\pi})} + \eta . \tag{10}$$

Thus,

$$K(t) \to \frac{1}{\pi}\int_0^{\epsilon_2} d\eta\, \frac{\tilde{\Phi}_1(\eta)}{\tilde{\Phi}_0^2(\eta) + \tilde{\Phi}_1^2(\eta)} e^{-\eta t} . \tag{11}$$

Under case A (the "normal" case) the principal contribution to $K(t)$ is

$$K(t) \to \frac{1}{\pi \tilde{\Phi}_0^2(0)} \int_0^{\epsilon_2} d\eta\, \tilde{\Phi}_1(\eta) e^{-\eta t}, \tag{12}$$

from which we deduce

$$\text{case A: } \Phi(t) \to -\Phi^2(0) K(t), \quad t \to \infty \tag{13}$$

which, along with the trivial relation [see Eq. 2]

$$\left[\int_0^\infty K(t)\,dt\right]\left[\int_0^\infty \Phi(t)\,dt\right] = 1 = \tilde{K}(0)\tilde{\Phi}(0), \tag{13a}$$

are our most important results. Thus, the acf and the mf have opposite sign and common functional behavior at long times. Their areas are related simply. In the specific case of the velocity acf, we have[4]

$$\Phi(t) \to -[(m/k_B T) D_s]^2 K(t), \quad t \to \infty \tag{14}$$

in conventional notation. In case $A_0$ [vanishing $\tilde{\Phi}(0)$] we expect $\Phi$ to vanish more rapidly than $K$, while in case B [infinite $\tilde{\Phi}(0)$] we expect the reverse We shall consider the latter through a special example.

Suppose that

$$\left.\begin{aligned} \Phi_0(t) &= a t^{-\alpha} + O(e^{-\epsilon t}) && (4a)\\ \tilde{\Phi}_0(s) &= \frac{a\Gamma(1-\alpha)}{s^{1-\alpha}} + g(s) && (5a) \end{aligned}\right\} (0 < \alpha < 1)$$

with $\alpha$ real and $g(0) \neq 0$. Then, the estimate in Eq. (11) continues to hold for $K(t)$, with

$$\tilde{\Phi}(\eta e^{\pm i\pi}) = \frac{a\Gamma(1-\alpha)}{\eta^{1-\alpha}} (e^{\mp(1-\alpha)\pi i}) + g(-\eta)\,. \tag{15}$$

One computes, using Eq. (15),

$$K(t) \to -\frac{1-\alpha}{\pi a} \frac{\sin\pi(1-\alpha)}{t^{2-\alpha}}\,, \tag{16}$$

$$K(t) \to -\frac{1-\alpha}{\pi a^2} \frac{\sin\pi(1-\alpha)}{t^{2-2\alpha}} \Phi(t)\,, \tag{17}$$

"faster," as expected. Also, Eq. (13a) does not apply. The requirement that $\alpha$ be real can be relaxed [though $\Phi(t)$ remains real] and leads to a longer calculation. The long-time behavior of $\Phi$ and $K$ is oscillatory,

$$\Phi(t) \sim c_1 t^{-\alpha_0} \cos(\beta_0 \ln t + c_2),$$

by hypothesis, and one can show easily that $|K(t)| < t^{-(2-\alpha_0)}$.

We have dealt so far only with the case of the dominant singularity lying at $s = 0$. Suppose, instead, that the $t \to \infty$ behavior is regulated by a pair of branch points lying at $s = \pm i\omega$ and that $\tilde{\Phi}(s)$ has case A behavior near the singularities. The function pair

$$\Phi_0(t) = b \frac{e^{i\omega t}}{t^{\alpha+i\beta}} + b^* \frac{e^{-i\omega t}}{t^{\alpha-i\beta}} + O(e^{-\epsilon t})\,, \tag{18a}$$

$$\tilde{\Phi}_0(s) = b \frac{\Gamma(1-\alpha-i\beta)}{(s-i\omega)^{1-\alpha-i\beta}} + b^* \frac{\Gamma(1-\alpha+i\beta)}{(s+i\omega)^{1-\alpha+i\beta}} \tag{18b}$$

provide an illustration. Note that $\Phi_0(t)$ describes an oscillatory approach to zero (equilibrium), as opposed to the damped approach of example (4a). We return to the general case where, for $t \to \infty$, we have

$$K(t) \sim \frac{1}{2\pi i} \int_0^\infty d\eta\, e^{-\eta t} \left[ e^{i\omega t} \left( \frac{\Phi_+(\eta) - \Phi_-(\eta)}{\Phi_+(\eta)\Phi_-(\eta)} \right) + e^{-i\omega t} \left( \frac{\Psi_+(\eta) - \Psi_-(\eta)}{\Psi_+(\eta)\Psi_-(\eta)} \right) \right], \tag{19}$$

where

$$\tilde{\Phi}(i\omega + \eta e^{\pm i\pi}) = \Phi_\pm(\eta), \quad \tilde{\Phi}(-i\omega + \eta e^{\pm i\pi}) = \Psi_\pm(\eta)\,. \tag{20}$$

Since $\Phi(s)$ is real when $s$ is real, we infer that $\Phi_+^*(\eta) \equiv \Psi_-(\eta)$, and $\Phi_-^*(\eta) \equiv \Psi_+(\eta)$. Then

$$K(t) \sim \frac{1}{\pi} \int_0^\infty d\eta\, e^{-\eta t} \operatorname{Im}\left[ e^{i\omega t} \left( \frac{\Phi_+(\eta) - \Phi_-(\eta)}{\Phi_+(\eta)\Phi_-(\eta)} \right) \right] \sim \frac{1}{\pi} \operatorname{Im}\left( \frac{e^{i\omega t}}{\Phi_+(0)\Phi_-(0)} \int_0^\infty d\eta\, e^{-\eta t} [\Phi_+(\eta) - \Phi_-(\eta)] \right), \tag{21}$$

while

$$\Phi(t) \sim -\frac{1}{\pi} \operatorname{Im}\{e^{i\omega t} \textstyle\int_0^\infty d\eta\, e^{-\eta t} [\Phi_+(\eta) - \Phi_-(\eta)]\}\,. \tag{22}$$

Since

$$\Phi_+(0)\Phi_-(0) = \tilde{\Phi}^2(i\omega) = A e^{i\varphi},$$

the relation between $K(t)$ and $\Phi(t)$ is not as simple as before; the asymptotic functional forms, though similar, differ in phase as well as amplitude.

As a final point, let us compare the mf

$$K(t) = \langle \dot{u} e^{it(1-P)L} \dot{u} \rangle \tag{23}$$

with the related acf

$$k(t) = \langle \dot{u}\, e^{itL} \dot{u} \rangle = -\frac{d^2}{dt^2} \Phi(t)\,, \tag{24}$$

where

$$\Phi(t) = \langle u e^{itL} u \rangle\,. \tag{25}$$

Our analysis makes it possible to compare the long-time behaviors of $k(t)$ and $K(t)$. One sees that in the (normal) case A these functions differ by two powers of $t$, $k(t)$ falling to zero more rapidly. This result is of some interest in the theory of Brownian motion.[5]

ACKNOWLEDGMENT

It is a pleasure to acknowledge a valuable conversation with Professor J. Miklowitz.

*Work supported in part by the National Science Foundation, under Grant No. GP-9626.

[1](a) R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, W. B. Downs, and J. Downs (Interscience, New York, 1961), Vol. 3; (b) B. J. Berne, in *Physical Chemistry*, edited by H. Eyring, D. Henderson, and W. Jost (Academic, New York, 1971).

[2]B. J. Adler and T. E. Wainwright, Phys. Rev. A 1, 18 (1970).

[3]G. Doetsch, *Handbuch der Laplace-Transformation* (Verlag, Basel, 1955), Vol. II.

[4]N. Corngold and J. Duderstadt, Phys. Rev. A 2, 836 (1970).

[5]P. Mazur and I. Oppenheim, Physica 50, 241 (1970).

PHYSICAL REVIEW A VOLUME 6, NUMBER 4 OCTOBER 1972

# Field Dependence of Gaseous-Ion Mobility: Theoretical Tests of Approximate Formulas*

Hong-sup Hahn and E. A. Mason
*Brown University, Providence, Rhode Island* 02912
(Received 16 March 1972)

Four approximate formulas, due to Wannier, Kihara, Frost, and Patterson, for the field dependence of ion mobility are tested by comparison with special cases for which accurate theoretical results can be found. The Kihara result, an expansion in $(E/N)^2$, has only limited range. The Frost-Patterson formulas at high fields apply only to rigid-sphere cross sections. The Wannier free-flight theory yields a formula with one parameter that can be chosen once and for all to fit the zero-field Chapman-Enskog result; without further adjustable constants the formula gives reasonable results at medium and high fields (largest deviations less than 20% in the special cases tested), and is applicable to any ion-neutral mass ratio and force law, including the case of resonant charge transfer.

## I. INTRODUCTION

It is well known that the drift velocity of an ion in a neutral gas depends on field strength. No general expression for the field dependence is known, although several approximate formulas have been suggested. The purpose of this paper is to test these approximate formulas by comparison with several accurate theoretical results for special cases, and to suggest a connection formula that can be used at all fields for all ion-neutral interactions. The most extensive test occurs for the case of light ions and heavy neutrals (Lorentzian mixture), for which the drift velocity can be found at all fields by numerical integration.

Dimensional arguments suffice to show that the drift velocity $v_d$ depends on the electric field strength $E$ and on the number density of the gas $N$ only through the ratio $E/N$. At low fields, $v_d$ is directly proportional to $E/N$ for all ion-neutral interactions, and is given by the Chapman-Enskog kinetic theory. At high fields the nature of the ion-neutral interaction determines the dependence of $v_d$ on $E/N$; for example, it is known that $v_d$ varies directly as $E/N$ for an $r^{-4}$ interaction potential and as $(E/N)^{1/2}$ for a rigid-sphere interaction.[1,2]

## II. APPROXIMATE FORMULAS

In this section we briefly outline four formulas which give $v_d$ as a function of $E/N$.

### A. Wannier Free-Flight Theory

In 1953 Wannier[2] indicated how to obtain a simple interpolation formula for $v_d$. Since his result has been almost universally overlooked, we indicate the line of arguments leading to it. An ion of mass $m$ and charge $e$ undergoes an acceleration $eE/m$ between collisions. If the ion lost all its momentum on every collision, the drift velocity would be $(eE/m)\tau$, where $\tau$ is the mean time between collisions; but the ion loses only a fraction of its momentum on each collision. The mass dependence of the momentum loss on collision can be calculated from the equations of momentum and energy conservation; if we average this momentum loss over all collisions and ignore subtleties about the average of a product and the product of the averages, we obtain

$$v_d = \xi\,(1+m/M)(eE/m)\tau\,, \tag{1}$$

where $M$ is the mass of a neutral molecule and $\xi$ is a factor of order unity that may depend in a complicated way on the ion-neutral force law and the masses $m$ and $M$. The mean free time is given by

$$\tau = 1/N\bar{v}_r Q\,, \tag{2}$$

where $\bar{v}_r$ is the mean relative speed of ions and neutrals and $Q$ is the average momentum-transfer cross section. It is reasonable to take $\bar{v}_r$ as the root-mean-square speed,