

Connection of the Velocity Autocorrelation Function to the Mean-Square-Displacement and to the Memory Function of Generalized Master Equations

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General connections between the velocity autocorrelation function and the mean-square-displacement for a special initial condition are established and shown to reduce in the high-temperature limit to earlier such results obtained by Scher and Lax. A simple and useful relation, which is valid in the high temperature limit, between the velocity autocorrelation function and memory functions in generalized master equations is given.

1. Introduction

This paper and a following one [1] are addressed to two related questions, a formal one of general relevance to transport theory, and a practical one concerning an important class of experiments [2–4] being carried out recently. The formal question is: what connections, if any, exist between the velocity autocorrelation function which is of importance to the calculation of such quantities as the conductivity on one hand, and the mean-square-displacement and memory function, which are relevant to motion in real space on the other? The practical question is: what is the d.c. and a.c. conductivity of photo-excited electrons in low mobility organic crystals such as naphthalene and anthracene?

The formal question is of obvious interest. It has been raised, at least in part, in a number of papers [5–10] treating conduction in disordered solids. Scher and Lax [8] have made their answer the basis of a successful theory of impurity conduction in disordered semiconductors. Our own answer contains a generalization of the results of [8] including correction terms which are non-zero at finite temperatures and which may have practical importance for conduction in the organic crystals mentioned above. In our calculation we start from linear response theory [11] and encounter no problems connected with the definition of the current operator in a localized basis [9, 10].

The practical question concerns measurements [2–4,

12, 13] of photoconductivity in organic crystals. In anthracene [12, 13], which serves as a model substance for organic materials, this quantity is nearly temperature independent between 400 K and 100 K. Recent measurements in single crystals of naphthalene [2–4] show a similar behaviour of photoconductivity between 300 K and 100 K. Below 100 K, however, photoconductivity in the c' - [2–4] and also in the b -direction [4] of the crystal increases exponentially. The importance of the experiments being carried out on these low-mobility organic molecular crystals stems from the challenging problems that they have been setting for the theorist and the detailed probing of the concept of small polaron motion that they appear capable of achieving. Thus, for instance, the drastic change in mobility with decreasing temperature is attributed to a transition from hopping to band motion, long expected theoretically [14–17]. The basic nature of this problem has caused a flurry of recent theoretical activity in this field [18–22].

In this paper, we shall answer the formal question posed above. In the following paper [1] we show how the answer to this formal question, when applied to organic molecular crystals, results in a specific prediction for the a.c. conductivity.

2. Connection of the Velocity Autocorrelation Function to Other Quantities

2.1. Basic Definitions and Relations

The velocity autocorrelation function $\psi_{vv}(t) = \text{Tr} \rho \{ \hat{v}(0), \hat{v}(t) \}$, with the curly brackets denoting as

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usual half the symmetrized product, derives its practical importance from Kubo's result [11] that its Fourier transform is closely related to the complex, frequency-dependent conductivity $\sigma(\omega)$. The latter is defined as the ratio of the two-sided Fourier transforms of the observed current and the applied field: $\sigma(\omega) = j(\omega)/E(\omega)$. Its real part $\sigma'(\omega)$ and imaginary part $\sigma''(\omega)$ are related to $\psi_{vv}(t)$ through

$$\sigma'(\omega) = \frac{1}{2} f(\omega); \quad \sigma''(\omega) = \mathcal{P} \int \frac{d\omega'}{\pi} \frac{\sigma'(\omega')}{\omega' - \omega}. \quad (2.1)$$

$$f(\omega) = E_\beta(\omega)^{-1} \int_{-\infty}^{\infty} dt e^{-i\omega t} \psi_{vv}(t). \quad (2.2)$$

The universal prefactor $E_\beta(\omega) = (\hbar\omega/2) \coth(\beta\hbar\omega/2)$ reduces in the high temperature limit to $\beta^{-1} = kT$ yielding the simple form ($\epsilon = 0^+$)

$$\sigma(\omega) = \beta \int_0^{\infty} dt e^{-i\omega t - \epsilon t} \psi_{vv}(t). \quad (2.3)$$

As is well known, the above results [11] are valid to first order in the electric field and assume that the system is in a canonical equilibrium density matrix $\rho = \exp(-\beta H)/\text{Tr}(\exp(-\beta H))$, where H is the Hamiltonian of the system before the application of an electric field.

In a localized description of conductivity it is more convenient to express the velocity correlation function by the site correlation function $\psi_{xx}(t)$. With the definitions of the velocity operator \hat{v} and of the canonical density operator ρ one arrives at

$$\psi_{vv}(t) = -\frac{d^2}{dt^2} \text{Tr} \rho \{ \hat{x}(0), \hat{x}(t) \} = -\frac{d^2}{dt^2} \psi_{xx}(t). \quad (2.4)$$

Using the cyclic property of the trace one shows that $\text{Tr} \rho \hat{x}(t)^2$ is time independent and transforms (2.4) to

$$\psi_{vv}(t) = \frac{1}{2} \frac{d^2}{dt^2} \text{Tr} \rho (\hat{x}(t) - \hat{x})^2. \quad (2.5)$$

Equation (2.5) is a result obtained by Scher and Lax [8], although they have exhibited it in a different form.

2.2. Connection of $\psi_{vv}(t)$ to Generalized Master Equations

Let us from now on consider the system to consist of N identical charge carriers such as electrons, assumed non-interacting, so that the various expressions written so far may be interpreted as single particle ones. The position operator is then

$$\hat{x} = \sum_n n |n\rangle \langle n| \quad (2.6)$$

where n labels the molecular site. Scher and Lax [8] have further reduced (2.5) to

$$\psi_{vv}(t) = \frac{1}{2} \frac{d^2}{dt^2} \sum_{m,n} (m-n)^2 P(m, t|n, 0) f_n \quad (2.7)$$

where $P(m, t|n, 0)$ is the probability that the m -th site would be occupied at t by a charge carrier if it occupied the n -th site at $t=0$, and f_n is $\langle n|\rho|n\rangle$, the site-diagonal element of the equilibrium density matrix. This result connects the velocity autocorrelation function to the mean-square-displacement, if f_n is taken to be independent of n .

Equation (2.7) is an *approximate* consequence of (2.5) and the missing terms that we shall supply below constitute one of the primary results of our paper. However, we first show an interesting and useful consequence of the approximate equation (2.7). We shall establish a connection between the velocity autocorrelation function and memory functions $\mathcal{W}_{mn}(t)$ appearing in generalized master equations [23]. The latter have the form [24, 25]

$$\frac{dP_m(t)}{dt} = \int_0^t dt' \sum_n (\mathcal{W}_{mn}(t-t') P_n(t') - \mathcal{W}_{nm}(t-t') P_m(t')). \quad (2.8)$$

Consider for simplicity that the system is translationally invariant. This gives $f_n = N^{-1}$ and $P(m, t|n, 0) = P_{m-n}(t)$. Kenkre has derived a result [26] connecting the mean-square-displacement in a periodic crystal and the memory functions. It is

$$\frac{d}{dt} \langle m^2(t) \rangle = - \int_0^t dt' \left(\frac{\partial^2 \tilde{\mathcal{W}}(k, t')}{\partial k^2} \right)_{k=0}, \quad (2.9)$$

where $\tilde{\mathcal{W}}(k, t) = \sum_m \mathcal{W}_m e^{ikm}$ and $\mathcal{W}_m = \mathcal{W}_{i,1+m}$. As the second derivative of $\langle m^2(t) \rangle$ is proportional to $\left(\frac{\partial^2 \tilde{\mathcal{W}}(k, t)}{\partial k^2} \right)_{k=0}$ from (2.9), and to $\psi_{vv}(t)$ from (2.5), we observe that

$$\psi_{vv}(t) = -\frac{1}{2} \left(\frac{\partial^2 \mathcal{W}(k, t)}{\partial k^2} \right)_{k=0}. \quad (2.10)$$

This is a simple and very useful relation between the velocity correlation function and memory functions. We now return to (2.7) and remark, as has been done also in [8] that it is an approximate relation requiring for its derivation the assumption that the equilibrium density matrix $\rho = \exp(-\beta H)/\text{Tr}(\exp(-\beta H))$ appearing in (2.4) is diagonal in the site representation. We point out that this assumption, if used

without proper care, leads to an absurd result. Thus, if the equilibrium ρ is diagonal in the site representation, it commutes with \hat{x} (which is also diagonal in the site representation). This means that the additive part of the Hamiltonian representing the applied field at the very first stage of Kubo's response theory [11] commutes with ρ . The autocorrelation function is then identically zero! This may be seen quite clearly from the original Kubo expressions [11] for the conductivity which involve the combination $\text{Tr} \hat{v} e^{iH} [\hat{x}, \rho] e^{-iH}$.

2.3. Connection of $\psi_{vv}(t)$ to Mean-Square-Displacement with Special Initial Conditions

We now show that it is possible to rewrite (2.5) exactly in a form which, while not identical to (2.7), is highly similar to it. In fact, $\psi_{vv}(t)$ will be seen to be proportional to the second time-derivative of the mean-square-displacement calculated for a specific initial condition which is not the localized condition corresponding to $P(m, t|n, 0)$ in (2.7). We start from the right hand side of (2.5) and using the representation (2.6) of the site operator \hat{x} as well as the completeness relation $1 = \sum_n |n\rangle\langle n|$, we arrive at

$$\begin{aligned} \text{Tr}(\hat{x}(t) - \hat{x})^2 \rho &= \sum_m 2m^2 \langle m|\rho|m\rangle \\ &- \sum_m \sum_n 2mn \langle m|e^{-i\mathcal{L}t} \{|n\rangle\langle n|, \rho\}|m\rangle. \end{aligned} \tag{2.11}$$

In this expression \mathcal{L} is the Liouville operator defined by $\mathcal{L}\dots = [H, \dots]$. The first sum in (2.11) may be further rewritten by using the completeness relation once more and the fact that ρ is the canonical density operator. In this way we get

$$\begin{aligned} \text{Tr}(\hat{x}(t) - \hat{x})^2 \rho &= \sum_m \sum_n (m-n)^2 \langle m|e^{-i\mathcal{L}t} \{|n\rangle\langle n|, \rho\}|m\rangle. \end{aligned} \tag{2.12}$$

This result transforms (2.5) into the remarkable form

$$\psi_{vv}(t) = \frac{1}{2} \frac{d^2}{dt^2} \sum_m \sum_n (m-n)^2 p_m^{(n)}(t). \tag{2.13}$$

Note that in this equation the quantity $p_m^{(n)}(t)$ given by

$$p_m^{(n)}(t) = \langle m|e^{-i\mathcal{L}t} \{|n\rangle\langle n|, \rho\}|m\rangle \tag{2.14}$$

plays the role of $P(m, t|n, 0) f_n$ in (2.7). Like the latter it is the diagonal element of an operator obeying the Liouville-von Neumann equation. It is also therefore the diagonal element of a density matrix and thus is the probability of occupation of m . However, while

$P(m, t|n, 0)$ is that probability for the initial condition that the n -th site is occupied, $p_m^{(n)}(t)$ is that probability for a different initial condition. The probability in (2.7) corresponds to the initial condition

$$\langle a|\tilde{\rho}(0)|b\rangle = \delta_{a,b} \delta_{a,n} \tag{2.15}$$

with $\tilde{\rho}(0) = \{|n\rangle\langle n|, \rho\}$, whereas that in (2.14) corresponds to

$$\langle a|\tilde{\rho}(0)|b\rangle = \frac{1}{2} \langle a|\rho|b\rangle (\delta_{a,n} + \delta_{b,n}). \tag{2.16}$$

Note that ρ on the right hand of (2.16) is $\exp(-\beta H)/\text{Tr}(\exp(-\beta H))$ from the original Kubo expression [11].

Before finishing this section we mention that its results may be derived without assuming the special representation (2.6) of the site operator. This generalization is given in the Appendix.

3. Concluding Remarks

Equation (2.13) is the primary result of this paper. Like the approximate relation (2.7), our exact (2.13) also states the proportionality of the velocity autocorrelation function to the second time derivative of the mean-square-displacement. The latter is, however, to be calculated for the perhaps surprising initial condition (2.16). It is important to stress here that neither the earlier approximate (2.7) nor the new exact (2.13) uses $\tilde{\rho}(0) = \exp(-\beta H)/\text{Tr}(\exp(-\beta H))$ as the initial condition for the calculation of the mean-square-displacement. That would lead to a vanishing result. The approximate (2.7) uses for its initial condition (2.15), which corresponds physically to placing a charge carrier at n . The exact (2.13) uses (2.16) which is obtained from $\rho = \exp(-\beta H)/\text{Tr}(\exp(-\beta H))$, by erasing all its elements except those in the n -th row and the n -th column. The approximation (2.15) corresponds to further erasing all the elements except the single one at the intersection of the n -th row and the n -th column. For high temperatures, when the diagonal initial condition used in (2.7) is justified, the autocorrelation function $\psi(t)$ is identical with the second derivative $\partial^2 \tilde{W}(k, t)/dk^2|_{k=0}$ of the memory function. This simple connection (2.10) between $\psi_{vv}(t)$ and the memory function does not hold in the general case. This is as it should be, since $\psi_{vv}(t)$ contains more information than merely the evolution of the diagonal elements of $\rho(t)$ in the site representation whereas memory functions are concerned only with that evolution. Needless to say, this statement does not preclude the possibility that future investigations might result in further connections between velocity autocorrelation functions and the time evolution of the diagonal elements of the density

matrix corresponding to the *particular* initial $\rho = \exp(-\beta H)/\text{Tr}(\exp(-\beta H))$.

A final comment concerning the assumption (2.6) that the position operator is diagonal in the representation of states $|n\rangle$ is in order here. That assumption is exactly valid for particles such as Frenkel excitons which exist only on lattice sites and not between them and valid as a good approximation for particles such as electrons in low-mobility crystals, which we are interested in. It is not valid for electrons in metals. However, it can be shown that all the above results hold independently of (2.6) and are therefore generally valid. The details of this demonstration are in the Appendix.

In a following paper [1] the results obtained here will be used in order to derive explicit expressions for the d.c. and a.c. photoconductivity in organic molecular crystals.

Appendix

Expressing the left hand side of (2.11) by a symmetrized product of δ -functions gives:

$$\text{Tr}(\hat{x}(t) - \hat{x})^2 \rho = \int dx \int dx_0 (x - x_0)^2 \text{Tr} \{ \delta(\hat{x}(t) - x), \delta(\hat{x}(0) - x_0) \} \rho \quad (\text{A.1})$$

$$= \int dx \int dx_0 (x - x_0)^2 \text{Tr} \delta(\hat{x} - x) e^{-i\mathcal{L}t} \{ \delta(\hat{x} - x_0), \rho \} \quad (\text{A.2})$$

where $\mathcal{L} \dots = [H, \dots]$ is the Liouville operator of the unperturbed problem. For translational invariance the expectation value depends only on $(x - x_0)$. Shifting the origin of the coordinate system and evaluating a δ -function, we arrive at

$$\text{Tr}(\hat{x}(t) - \hat{x})^2 \rho = \text{Tr} \hat{x}^2 e^{-i\mathcal{L}t} \{ \delta(\hat{x}), N \rho \}, \quad (\text{A.3})$$

where $N = \int dx$ is determined from normalization. Equation (A.3) shows that $\text{Tr}(\hat{x}(t) - \hat{x})^2 \rho$ represents the time dependent mean-square-displacement calculated with a density operator

$$\tilde{\rho}(t) = e^{-i\mathcal{L}t} \{ \delta(\hat{x}), N \rho \}. \quad (\text{A.4})$$

Herein ρ is the canonical distribution. The initial condition for this density operator is

$$\tilde{\rho}(0) = \{ \delta(\hat{x}), N \rho \} = \frac{N}{2} (\delta(\hat{x}) \rho + \rho \delta(\hat{x})) \quad (\text{A.5})$$

Equation (A.5) is a generalization of (2.13–2.16) in the text and we thus see that (2.6) is not required as an assumption.

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