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THE GENERALIZED MASTER EQUATION AND ITS APPLICATIONS*

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I. INTRODUCTION

The generalized master equation (GME) is an entity one meets with on the wayside in one's journey from the microscopic to the macroscopic level of the dynamics of large systems in statistical mechanics. The prominent character in this journey is *not* the GME but is the Pauli master equation (PME) also known as *the* Master equation. The latter, with its distinctive tendencies as are evident in the H-theorem and its generally built-in irreversibility, possesses the ability to guide the weary [*1*] traveller safely (?) to the realm of macroscopic phenomena. The importance of

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the GME is therefore not always appreciated in the normal course of this journey. In fact, usually, the equation is not even allowed to live long. Almost immediately after one makes its acquaintance, a procedure known as the Markoffian approximation [2] is thrust into the GME, destroying its special characteristics and converting it into the sought-after PME. There are, however, researchers, who admire the GME for its own qualities (and not merely for its ability to give birth to the PME), who have recently studied it in its own right and have put to use its potentialities. This article will trace some of this activity concerning this interesting, powerful, but not always appreciated equation.

The connections of this subject to Elliott Montroll are three: as everyone knows he is a confirmed traveller [3] and has made numerous contributions to the clearing of the path in the journey of statistical mechanics mentioned above; he was one of the first to meet with the GME, having used for the purpose his favorite conveyance, the determinants [4]; and he belongs to the group of people who love the GME for its own traits. It is a pleasure therefore to dedicate this article to him on the occasion of his sixtieth birthday.

II. HOW THE GME IS BORN

The central task of nonequilibrium statistical mechanics consists of bridging the gap between the microscopic and the macroscopic equations of motion of large bodies. Large-scale phenomena exhibit approach to equilibrium, irreversibility,and closure, although the underlying dynamics at the microscopic level has recurrences, is totally reversible,and involves an enormously larger number of variables pertinent to the zillions of constituent particles. Much work has been done in an attempt to resolve this seemingly paradoxical situation [5]. Beginning with Boltzmann, many have made important contributions to this activity and, although the problem is far from being completely solved, a certain degree of understanding has been achieved. The work of van Hove [6,7] is one of those important contributions. With the Schroedinger equation as his point of departure he showed how, under a certain limiting process known as the λ^2 t limit", the PME may be obtained for the evolution of the probabilities of occupation

in a given basis provided the basis, and the system in general, obey certain mathematical conditions. The $\lambda^2 t$ limit includes the "weak-coupling" assumption that the perturbation, which is the cause of the evolution in the given representation, is small. While examining the consequences of relaxing this weak-coupling assumption, van Hove and collaborators found [7] that the result of their procedure was not the PME but an equation that, although formally similar to the PME, was non-local in time. It was thought [8] at the time that the other assumptions, conditions, and procedures of van Hove were necessary to obtain the new equation. Swenson however showed [9] that they were not and that the non-local equation (not the PME!) was an exact consequence of the Schroedinger equation under a certain class of initial conditions. Several others among them Prigogine and Résibois [10], Nakajima [11], Zwanzig [12,13], and Montroll [4], obtained formally similar equations. A significant service to workers in statistical mechanics was rendered by Zwanzig [13] who gave a clear analysis of the relations among the various derivations, and the equation

$$\frac{dP_M(t)}{dt} = \int_0^t dt' \sum_N [W_{MN}(t-t')P_N(t') - W_{NM}(t-t')P_M(t')] \tag{1}$$

for the evolution of the probability P_M of occupation of the state M, was thenceforth called the generalized master equation. The term "generalized" is used to distinguish it from *the* Master equation (or the PME)

$$\frac{dP_M(t)}{dt} = \sum_N [F_{MN}P_N(t) - F_{NM}P_M(t)] \tag{2}$$

which is local (in time) and exhibits approach to equilibrium. Equation (1) is evidently non-local and the nature of the "memory functions" $W(t)$ determines whether or not (and how) the system described by it equilibrates. The relations between equations (1) and (2) are two. The first is that the former is converted into the latter by the "Markoffian approximation"

$$W_{MN}(t) = F_{MN}\delta(t) \tag{3}$$

alluded to in Section I. The second is that there exists a class of W's for which the solutions of equation (1) tend to those of equation (2) for sufficiently long times [14].

We have stated above that the GME [equation (1)] can be obtained in several different ways from the microscopic equations of motion. Since an analysis of the relations of these various ways to one another exists in the literature [13], we shall focus on only one of them, viz. that due to Zwanzig [12]. The Schroedinger equation, when prepared for the activities of statistical mechanics, dons the form

$$i \frac{\partial \rho}{\partial t} = [H, \rho] = L\rho \tag{4}$$

and assumes the name Liouville - von Neumann. Here ρ is the density matrix, L is the Liouville operator, H is the Hamiltonian and $\hbar$ is equal to 1. The projection technique [12] is especially designed to take one quickly from the microscopic starting point [equation (4)] to the GME [equation (1)] with the minimum amount of effort. The probability P_M in the GME is identified with the diagonal element $\langle M|\rho|M\rangle$ of the density matrix ρ in the representation of states $|M\rangle, |N\rangle$, etc. This representation is that of the eigenstates of H_0, a part of the total Hamiltonian H:

$$H = H_0 + \lambda V \ . \tag{5}$$

Here λV is the perturbation causing the evolution in the space of the H_0 eigenstates, λ being a c-number denoting the strength of the interaction. The projection technique proceeds in three steps: (i) the definition of the projection operator P which, when allowed to operate on any operator O, extinguishes all its elements which are off-diagonal in the representation of the H_0 eigenstates:

$$\langle M|PO|N\rangle = \langle M|O|M\rangle \delta_{M,N} \tag{6}$$

(ii) the successive application of P and $(1-P)$ to equation (4) resulting in two simultaneous equations for $P\rho$ and $(1-P)\rho$, and (iii) the trivial elimination of $(1-P)\rho$ by Laplace-transforms or otherwise [15]. The result of these three steps is a quasi-closed equation for $\rho' \equiv P\rho$, the diagonal part of the density matrix:

$$\frac{\partial \rho'}{\partial t} = \int_0^t dt' \; K(t-t')\rho'(t') + I(t) \qquad (7)$$

where $I(t)$ and the "super-operator" kernel $K(t)$ are given by

$$I(t) = iPLe^{-it(1-P)L}(1-P)\rho(0) \qquad (8)$$

$$K(t) = -PLe^{-it(1-P)L}(1-P)L \quad . \qquad (9)$$

The first term in equation (7) is dependent *only* on ρ' although it involves it at all times t' in the past. It is thus "closed" in ρ'. The second term of equation (7) does depend on the off-diagonal part of ρ but, as equation (8) shows, the dependence is only on the *initial* value (at t=0) of this off-diagonal part and is thus formally simple. Furthermore $K(t)$ and $I(t)$ are obtainable in principle as system entities and *are not dependent* on $\rho'(t)$. Finally, whenever ρ is initially diagonal, $I(t)$ becomes identically zero *for all times*, making equation (7) truly closed in ρ'. It is for these reasons that equation (7) has been termed quasi-closed in ρ'.

If the initial diagonality condition on ρ holds, the M-th element of equation (7) *is* the generalized master equation [equation (1)]. We have thus seen how the GME is obtained from the microscopic dynamics. It is important to realize that the initial diagonality assumption is a condition and not necessarily an approximation, and that under it the GME is an *exact* consequence of the microscopic dynamics. We emphasize this point because even now, more than fifteen years since these analyses were first published, it is often not realized that a closed (albeit non-local) equation for the *probabilities* can be an exact consequence of *quantum* mechanics.

III. HOW THE GME GROWS

There are two reasons why one might attempt to modify the derivation of the GME given in the previous section. The first is conceptual and the second practical. Both reasons stem from one's dissatisfaction with the identification of the probability P_M with $\langle M|\rho|M\rangle$, the diagonal

element of the density matrix. The dissatisfaction has its source in the fact that a macroscopic description is perforce much coarser than a microscopic one, and its states M must therefore be correspondingly coarser versions, i.e. groups, of the microscopic states $|M\rangle$. As emphasized by Uhlenbeck [5], van Kampen [16], and others, this coarsening of the description is an important feature of the passage from the microscopic to the macroscopic level of dynamics. It is not represented at all in the previous derivation. One therefore wishes to derive an evolution equation which directly governs the time dependence not of the diagonal element of ρ, but of a sum of such diagonal elements. Specifically, if one now represents the eigenstates of H_0 by $|\xi\rangle, |\mu\rangle$, etc., and reserves the labels M, N, etc. for groups of those eigenstates, one can make the identification

$$P_M = \sum_{\xi \epsilon M} \langle \xi | \rho | \xi \rangle \tag{10}$$

which incorporates the feature of the passage from microscopics to macroscopics mentioned above. In addition to the conceptual need for this coarse-graining there is also a practical one. In transport calculations one is often interested in an extremely small part of the system. Thus one may wish to get rid not only of a "heat-bath" but even of the phonons in an electron-phonon system and to concentrate on the evolution of (for instance) the *two* electron states in a dimer. These considerations require a generalization of the projection operator of the previous section. Such a generalization was first made by Emch [17] for the conceptual reasons explained above and independently, but much later, by the author [18] for practical transport calculations. Our version of this Emch generalization of the Zwanzig projection operator may be written as

$$\langle \xi | PO | \mu \rangle = \left[\sum_{\xi \epsilon M} \langle \xi | O | \xi \rangle \right] \left[\sum_{\xi \epsilon M} 1 \right]^{-1} Q_\xi \delta_{\xi \mu} \tag{11}$$

and should be compared to equation (6). The first factor on the right-hand-side of equation (11) represents the coarse-graining, the second makes the sum take the form of an average, the third is a weighting factor in the choice of which there is a certain latitude as explained below, and the last is the diagonalizing Kronecker delta. To

ensure that $P^2=P$, Q_ξ must satisfy

$$\sum_{\xi\epsilon M} Q_\xi = \sum_{\xi\epsilon M} 1 \equiv g_M \tag{12}$$

where g_M denotes the number of states in the grain M. This condition for idempotency of P can be derived directly from equation (11) by calculating $\langle\xi|P^2 0|\mu\rangle$ from it. Also, in practical calculations, particularly useful expressions result when Q_ξ is independent of the grain (not independent of ξ). However this can be arranged quite naturally in cases of interest. Thus, consider as in [*18*], a system of spins interacting with a bath of phonons. The system state is an outer product of the spin state and the phonon state: $|\xi\rangle=|M,m\rangle=|M\rangle|m\rangle$, the grains M corresponding to the spin states and the "space within the grains", represented by m, to the phonon states. In exciton transport [*19*] the exciton states are represented by $|M\rangle$ and the phonon states by $|m\rangle$. It is quite natural (and convenient) in these cases to write $Q_\xi=Q_m$ and thus ensure that it is independent of the grain M. In our earlier calculations [*18*,*19*] the choices $Q_m=1$ and $Q_m=[\exp(-\beta E_m)][\sum_m \exp(-\beta E_m)]^{-1}[\sum_m 1]$ have been used [*20*]. The former is appropriate to a microcanonical ensemble and the latter to a canonical one.

The above comments concerning Q_ξ might lead one to believe that there is considerable flexibility in the choice of the Q's. This is true only if one is willing to violate $(1-P)\rho(0)=0$ and either treat that initial condition as an *approximation* or undertake an analysis of the term $I(t)$ of equation (8). Otherwise $\rho(0)$ dictates the form of Q through the initial condition:

$$Q_\xi=[\langle\xi|\rho(0)|\xi\rangle][\sum_{\xi\epsilon M} \langle\xi|\rho(0)|\xi\rangle]^{-1}[\sum_{\xi\epsilon M} 1] \tag{13}$$

We thus see that the modified projection operator performs two operations in addition to diagonalization: it averages the diagonal elements in groups thus removing any variation within the grain; it then imposes its own variation Q_ξ.

The modification of P, as advocated in equation (11), does not change the form of the resulting equations (7), (8), (9) and finally the GME (1). However the meaning of the quantities $I(t)$, $K(t)$ and $W(t)$ is certainly changed as

the P's in them coarse-grain in addition to diagonalizing. The initial "diagonality" of ρ, which allows the transition from equation (7) to (1), also changes its meaning accordingly. One must now not only have no off-diagonal elements in the initial ρ, but must demand that, within each coarse grain or group, the variation of the diagonal elements with ξ is given precisely by Q_ξ. Equation (13) will clarify this last statement.

The effect of this modification on transport calculations will be described in the next section. Its effects on the irreversibility problem will be sketched in the appendix to this article. Here we shall show the resulting *approximate* prescriptions for evaluating the memories W_{MN} of equation (1).

An exact evaluation of $K(t)$ or $W_{MN}(t)$ is essentially tantamount to a full solution of the dynamics of the problem. It should be evident therefore that approximation techniques are necessary for all but the most unrealistically simplified situations. To this end Zwanzig introduced the weak-coupling approximation [*12*] whereby he replaced $(H_0+\lambda V)$ by merely H_0 in the term $[\exp\{-it(1-P)L\}]$ in equation (9) or (7) and showed that a simple formula resulted for W_{MN}:

$$W_{MN}(t) = 2|\langle M|\lambda V|N\rangle|^2 \cos(E_M-E_N)t \ . \tag{14}$$

Note that substituting equation (14) in equation (3) and integrating gives

$$F_{MN} = 2\pi|\langle M|\lambda V|N\rangle|^2 \delta(E_M-E_N) \tag{15}$$

which establishes the connection between the approximate form of the GME and the PME with the Golden Rule prescription of equation (15) for its rates.

In conjunction with our modified projection operator the weak-coupling approximation can be shown to yield

$$W_{MN}(t)=2 \sum_{\xi\epsilon M} \sum_{\mu\epsilon N} [Q_\mu/g_N]|\langle\xi|V|\mu\rangle|^2 \cos(E_\xi-E_\mu)t \tag{16}$$

$$W_{NM}(t)=2 \sum_{\xi\epsilon M} \sum_{\mu\epsilon N} [Q_\xi/g_M]|\langle\xi|V|\mu\rangle|^2 \cos(E_\xi-E_\mu)t \ . \tag{17}$$

Under the Markoffian approximation one puts $W(t) \approx \delta(t)[\int_0^\infty dt' W(t')]$ which reduces these equations to Golden Rule rate expressions. These, unlike equation (15), have the familiar average [21] over the initial state and summation over the final state, leading to the density-of-states factor.

The calculation behind equations (16) and (17) being quite straightforward we have never felt the need to publish it. However there has been some confusion about the emergence of the various factors in the final expressions and erroneous assumptions appear sometimes to have been made concerning, for instance, the inclusion of factors like Q_ξ *within* the summation in equation (11). We shall therefore briefly outline the calculation. In a manner completely analogous to Zwanzig's [12] one arrives at

$$\frac{\partial(P\rho)}{\partial t} = -\int_0^t dt' P L_V e^{-i(t-t')H_0} (L_V P\rho) e^{+i(t-t')H_0} \qquad (18)$$

wherein the argument of $P\rho$ is t in the left-hand-side and t' in the right-hand-side, and L_V denotes commutation with λV. Cancelling a factor (Q_ξ/g_M) from both sides of the ξ^{th} element of equation (18) and introducing $\sum_{\text{all } \mu} |\mu><\mu|$ as the identity [22], one obtains

$$\frac{\partial P_M}{\partial t} = \int_0^t dt' \sum_{\xi \in M} \sum_{\text{all } \mu} S_{\xi\mu}(t-t')[<\mu|P\rho|\mu> - <\xi|P\rho|\xi>] \qquad (19)$$

where $S_{\xi\mu}(t) = 2|<\xi|V|\mu>|^2 \cos(E_\xi - E_\mu)t$, and t' is the argument of ρ. Direct application of equations (11) and (10) shows the two-term factor in the summation in equation (19) to be $[(Q_\mu/g_N)P_N(t') - (Q_\xi/g_M)P_M(t')]$. Splitting the summation over all μ's into one within the grain N (to be absorbed in the memory expressions) and another over the grains N, equations (1), (16), and (17) immediately result.

IV. HOW THE GME IS PUT TO WORK

The special attraction of the GME is that, being less removed from, and consequently more loyal to, the Liouville-

von Neumann equation, it has a wider range of validity than the PME. In particular it contains short-time information not possessed by the latter. Microscopic oscillations, coherences, and other subtleties, to which the PME is totally blind, can therefore be sought and explored with its help. To appreciate the special powers of the GME which arise from its "non-Markoffian" (i.e. non-local) nature, observe that completely coherent transport as described by the classical wave equation and completely incoherent transport as described by the diffusion equation can be combined into the single equation

$$\frac{\partial P(x,t)}{\partial t} = \int_0^t dt' \; D(t-t') \; \frac{\partial^2 P(x,t')}{\partial x^2} \tag{20}$$

which is nothing other than the GME for a continuum with short range transitions. The choice $D(t)=D\delta(t)$ converts equation (20) into the diffusion equation while if $D(t)=c^2$ one recovers the wave equation. Here $P(x,t)$ is the probability, D the diffusion constant and c the speed of the wave. Complete absence of memory of past times thus corresponds to incoherent transport and perfect memory to coherent transport. Both extremes may be obtained from the GME in this way. Furthermore an intermediate memory, which is neither perfect nor totally absent, yields solutions of the GME which are coherent at short times but diffusive at large times. As an example note that the choice $D(t)=c^2\exp(-tc^2/D)$ converts equation (20) into

$$\frac{\partial^2 P(x,t)}{\partial t^2} + \left(\frac{c^2}{D}\right) \frac{\partial P(x,t)}{\partial t} = c^2 \frac{\partial^2 P(x,t)}{\partial x^2} \tag{21}$$

which is a form of the telegrapher's equation and which, as was well known to Heaviside, Kelvin and others [23], does produce waves which eventually damp out into diffusive transport.

This potentiality of the GME was directly used by Knox and the author [24] in the context of exciton transport. Transfer of electronic excitation in atomic or molecular aggregates is of importance to diverse fields such as sensitized luminescence and photosynthesis. Calculations of Perrin [25] based on wave-like transfer as would arise from the Schroedinger equation involving a small

number of states (for instance two) were unsuccessful in explaining experiments on fluorescence depolarization. Förster developed a successful theory based on incoherent transfer as described by the PME. The theory was later extended and elaborated upon by Dexter. Being based on the PME, this theory [*26*] is obviously unable to describe wave-like oscillations of the probability. Although such oscillations were never observed directly in luminescence experiments, coherent transport was invoked by some authors to explain some departures from the predictions of the Förster-Dexter theory [*26*]. The departures were in the context of the dependence of transfer rates on intersite distance. These rates, when calculated by the Fermi Golden rule, are proportional to the square of the matrix element of the interaction. Coherent rates were sometimes defined as being proportional to the matrix element itself. The latter being inversely proportional to the cube of the intersite distance R in the case of dipole-dipole interaction, coherent transport (sometimes called fast transport) was characterized by R^{-3} rates and incoherent motion by R^{-6} rates. Förster [*27*] stated the problem clearly and expressed the need for unifying the two descriptions. It was sometimes claimed that no relation could exist between them. However a connection can be established and a formalism capable of treating the intermediate case and of providing a continuous transition from the -3 exponent to the -6 one can be given as follows.

Considering for the sake of simplicity the GME for a linear chain with W_{MN}'s that factor into space parts F_{MN} and a time part $\phi(t)$

$$\frac{dP_M(t)}{dt} = \int_0^t dt'\phi(t-t') \sum_N [F_{MN}P_N(t')-F_{NM}P_M(t')] \qquad (22)$$

the author has shown [*28*] that homogeneity in space, characterized by $F_{MN}=F_{M-N}$, leads to the following equation for the mean square displacement $\overline{M^2}(t)=\sum_M M^2P_M(t)$:

$$\frac{d\overline{M^2}(t)}{dt} = <M^2>\int_0^t dt'\phi(t')+2<M>\int_0^t dt'\phi(t-t')\overline{M}(t') \qquad (23)$$

Here $<M^2>=\sum_M M^2F_M$, $<M>$ and $\overline{M}$ have obvious meanings and the

infinite extent of the chain has been used. For situations possessing no bias, the last term in equation (23) is zero and one has a simple relation between the mean square displacement and the memory $\phi(t)$. (Strangely enough, it has the appearance of Newton's second law of motion.) On the basis of this relation it is possible to define [*24*] a unified rate ω for coherent and incoherent transport by identifying it with the reciprocal of the time required for $\overline{M^2}$ to build up from the value 0 (taking initial localization on site 0) to the value 1. This signifies that in an average sense the excitation has moved a distance of one site. One then obtains

$$\int_0^{1/\omega} dt \int_0^t dt' \phi(t') = \frac{1}{\langle M^2 \rangle} . \tag{24}$$

Four comments will now be made about equation (24). The extreme choice $\phi(t)=\delta(t)$, which would make the GME a PME and would represent totally incoherent transport, results in $\omega = \langle M^2 \rangle$. The extreme choice $\phi(t)$=const. would represent totally coherent transport and results in $\omega^2 = (\text{const.}/2)\langle M^2 \rangle$. Expanding *any* memory at short times as $\phi(t)=\phi(0)+ \ldots$, and retaining only the first term, gives, *for short times* $\omega^2=[\phi(0)/2]\langle M^2 \rangle$. *Any* memory that eventually decays to zero, results *at long times* in $\omega = (\text{const.})^{-1}\langle M^2 \rangle$ where the constant equals $\int_0^\infty dt\phi(t)$.

These comments immediately show how a natural unification of the R^{-3} and R^{-6} rates can be made. Note here that $\langle M^2 \rangle$ is proportional to R^{-6} for dipole-dipole interactions and observe how it is proportional to the rate ω in one extreme and to ω^2 in the other. For the case of nearest neighbour interactions and an exponential memory: $\phi(t)=\alpha\exp(-\alpha t)$, Knox and the author [*24*] gave explicit expressions for ω and analyzed with their help, some data on bacteriochlorophyll-protein complexes.

The utilization [*19*] of our explicit coarsegrained formulae for the memory functions [equations (16) and (17)] in the context of exciton transport results in an interesting connection between transport parameters and spectral features of the system under study. This connection provides a useful prescription for extracting the memory functions from experimentally measurable quantities.

Briefly, $W_{MN}(t)$ is found to be the inverse Fourier transform of the real part of the product of the Fourier transforms of the lineshape functions for the optical *absorption spectrum* for the molecule at site M and for the *emission spectrum* for the one at site N. The detailed derivation of this result is in refs. [*19*]. Through this practical prescription we have compiled [*29*] the memory functions for various real systems and the results are useful in assessing the extent of coherence in those systems.

The coarse-grained formulae have also been applied by Rahman and the author [*19*] for model calculations in exciton transport and by the author [*18*] for describing the approach to equilibrium of certain ferromagnet models. Similar calculations have been given by O. Entin-Wohlman and Bergman [*30*] in the context of polaron motion. We have also used the formulae for analyzing oscillatory behavior observed in the Kac-Dresden ring models [*31*].

Among other recent uses of approaches closely related to the GME, we mention the work on charge transfer in amorphous systems [*32*] by Scher and Lax, and by Scher and Montroll, and the work on rotational relaxation in liquids [*33*] by Lindenberg and Cukier. The general subject of memory-function formalisms is vast and we do not review it here.

V. HOW THE GME RELATES TO OTHERS

The GME bears interesting relations to several other transport entities. We have seen how the PME emerges from it under the effect of the Markoffian approximation. Here we shall briefly explain its connection to continuous time random walks (CTRW) and to stochastic Liouville equations (SLE).

The regular discrete-time random walk described by

$$P_M(r\tau) = \sum_N Q_{MN} P_N(r\tau - \tau) \tag{25}$$

relating the probabilities of occupation at time $r\tau$ to those one discrete time interval τ earlier through the transition probabilities Q_{MN}, was generalized by Montroll

and Weiss [34] to continuous time situations. Their formulation is equivalent to

$$P_M(t)=P_M(0)\left[1-\int_0^t dt'\psi(t')\right]+\int_0^t dt'\sum_N Q_{MN}\psi(t-t')P_N(t') \tag{26}$$

where the "pausing-time distribution function" $\psi(t)$ describes how long the walker may pause at a site before taking the next step. Observe how the first term clearly represents the probability that the walker has lingered at M. Montroll, Shlesinger, and the author [14] showed that this Rip-van-Winkle behaviour of the CTRW is related to the memory of the simplified GME (22). Here we shall show the equivalence, first given by Knox and the author [35], of the general GME (1) and a natural extension of equation (26).

The Laplace transform of the GME (1) is

$$\varepsilon\tilde{P}_M-P_M(0) = \sum_N \tilde{w}_{MN}\tilde{P}_N - \sum_N \tilde{w}_{NM}\tilde{P}_M \tag{27}$$

where ε is the Laplace-variable and tildes denote the transforms. A rearrangement of equation (27) leads to

$$\tilde{P}_M=P_M(0)\left[\varepsilon+\sum_N \tilde{w}_{NM}\right]^{-1}+\left[\varepsilon \sum_N \tilde{w}_{NM}\right]^{-1}\sum_N \tilde{w}_{MN}\tilde{P}_N \tag{28}$$

which is inverted into

$$P_M(t)=P_M(0)\left[1-\int_0^t dt'\psi_M(t')\right]+\int_0^t dt'\sum_N Q_{MN}(t-t')P_N(t') \tag{29}$$

which is a natural generalization of equation (26) for cases wherein the pausing-time distribution function depends on the sites. The connection between the GME and the CTRW quantities is given by

$$\tilde{Q}_{MN} = \tilde{w}_{MN}\left[\varepsilon + \sum_N \tilde{w}_{NM}\right]^{-1} \tag{30}$$

$$\tilde{\psi}_M = \left[\sum_N \tilde{w}_{NM}\right]\left[\varepsilon + \sum_N \tilde{w}_{NM}\right]^{-1} \tag{31}$$

Various particular cases of these equations may be obtained [36]. For instance, for $W_{MN}(t)=F_{MN}\phi(t)$ one recovers

$$\frac{d\psi_M(t)}{dt}+\left[\sum_N F_{NM}\right]\int_o^t dt'\phi(t-t')\psi_M(t')=\left[\sum_N F_{NM}\right]\phi(t)+$$

$$+\psi_M(0)\delta(t) \quad (32)$$

Also, solving for $\tilde{W}$ from equations (30) and (31) above and identifying $\tilde{W}$ with $\tilde{K}$ of the first ref. [36] yields their equation (77), whereas writing M as (k,ℓ), where ℓ is an internal state and k a reciprocal space vector, gives equations (40) and (41) of the second ref. [36].

Transport equations for the density matrix which have a part having the Liouville-von-Neumann form and a part having the PME form have been termed "stochastic Liouville equations" by Kubo [37]. Such equations have been used by Haken and collaborators [38] and by Silbey and collaborators [39] in exciton transport and their relation to the GME was established by the author [40]. For a simple dimer consisting of two states 1 and 2, the equations

$$\frac{d\rho_{11}(t)}{dt} = -iJ(\rho_{21}-\rho_{12})+\int_o^t dt'A(t-t')[\rho_{22}(t')-\rho_{11}(t')] \quad (33)$$

$$\frac{d\rho_{12}(t)}{dt} = -iJ(\rho_{22}-\rho_{11})+\int_o^t dt'B(t-t')[\rho_{21}(t')-\rho_{12}(t')] \quad (34)$$

constitute a *generalized* SLE in that the last terms are non-local in time. Note the character of the two terms on the right-hand-side. The relation of these equations to the GME

$$\frac{d\rho_{11}(t)}{dt} = \int_o^t dt'W(t-t')[\rho_{22}(t')-\rho_{11}(t')] \quad (35)$$

is immediately obtained through Laplace transforms as

$$\tilde{W} = \tilde{A} + 2J^2[\varepsilon + 2\tilde{B}]^{-1} \ . \quad (36)$$

This two-term form is very interesting and shows that

ordinary SLE's with $A(t) = A\delta(t)$ and $B(t) = B\delta(t)$, are equivalent to a GME with a memory that is *the sum of a δ-function and an exponential*. For exciton transport the terms A and B are intimately related to different parts of optical spectra and we have studied them particularly in the context of zero-phonon lines in the last of refs. [*19*]. These issues will not be discussed here.

VI. WHITHER GME?

We have discussed above some aspects of this object which we find to be useful, powerful, exciting, and needlessly ignored. We wish not to make any prophetic remarks concerning its usefulness in the future but only to state that many interesting avenues of research regarding it still remain open. In the purely formal domain one is to derive useful expressions for $I(t)$, another to study the effects of $I(t)$ on the GME in the sense of a driving term, a third to explore consequences of structure in H_0 eigenstates on the coarse-grained formulae for W's.

APPENDIX
POOR MAN'S VERSION OF THE EXPLANATION OF THE ORIGIN OF IRREVERSIBILITY

Despite herculean efforts since the time of Boltzmann to clarify the origin of irreversibility and approach to equilibrium within a system of mechanics grounded in reversible equations of motion, a universally acceptable picture has not emerged. Much physical intuition has been accumulated on the basis of general arguments as well as of exact solutions of a highly limited number of simplified models. However many important issues remain open [*41*]. The actual situation among the workers in the field appears to be that each one develops his/her/its own private picture of this fascinating problem. Here, within the relative safety of an appendix, I shall venture to present, *very* briefly, such a private picture. The reader is warned that it is definitely incomplete, touches in a blurred way or not at all on some important issues, but he is assured that it is quite unpretentious, several of its elements being admittedly drawn from the ideas of others [*5,6,12,16,*

17, 42]. I include it here because I find it physically appealing and privately satisfying, in spite of its relatively low level of sophistication, and because it is based on the coarse-grained equations (16) and (17) given in the text.

After van Hove and others, let us remind ourselves that approach to equilibrium should not be universally obtained but only when we look (i) at a coarse level of description, (ii) at times that are not too long so that Poincaré recurrences can be forgotten or, alternatively, at systems that are large enough to possess recurrences occurring at times much larger than observation times, (iii) at sufficiently long times so that transient coherences can be avoided, and (iv) only at certain systems since not every system is dissipative. In van Hove's treatment [*6*], (i) corresponds to his choice of "smooth operators" allowing him to sum over many states, (ii) is taken care of by the thermodynamic limit, (iii) is ensured by a part ($t \to \infty$) of the $\lambda^2 t$ limit, and (iv) corresponds to the diagonal singularity conditions. We shall now see how an analysis from equation (16) or (17) can take into account (i) through (iv) in a simple way. We shall not invoke (iii) explicitly in that our GME can observe (and is proud to be able to) the transient coherences, which, however, we can avoid by looking at the asymptotic behaviour of the solutions. Also (i) is automatically ensured by the coarsegraining that is built into the projection operator defined to obtain equation (16) or (17).

Observe now that equation (16) or (17) *has the form of a Fourier transform.* Concentrating on the essentials and ignoring Q_μ and the μ-summation in equation (16), we write

$$W(t) = \int d\omega \cos\omega t \, Y(\omega) \qquad (A.1)$$

the ω-summation being the ξ-summation in equation (16) and $Y(\omega)$ being essentially the product of the matrix element of V, here to be symbolized by $|\langle|V|\rangle|^2$, and the density of states in the grain of the ξ's, to be symbolized by $f(\omega)$:

$$Y(\omega) = \text{const.} \, |\langle|V|\rangle|^2 f(\omega) \ . \qquad (A.2)$$

From equation (A.1) we observe that a simple oscillatory $W(t)$ arises from a singular $Y(\omega)$, and a decaying $W(t)$ from

a non-singular $Y(\omega)$. The problem before us may be considered to be that of understanding how the GME can become a PME, or, more precisely, how the passage from microscopics to macroscopics can change the character of the W's from oscillatory [see equation (14)] to that of a δ-function, the ultimate in decay [see equation (3)]. Equation (A.1) transfers this problem to that of understanding how $Y(\omega)$ changes its character from singular to non-singular. However this is displayed clearly in equation (A.2). A small system with well-spaced discrete states has a density of states $f(\omega)$ that is a clearly recognizable sum of δ-functions (in energy) and which is thus quite singular. The thermodynamic limit pushes those states closer together forming a continuum and, provided $|<|V|>|^2$ has no singularities, $Y(\omega)$ becomes non-singular, resulting in approach to equilibrium. Non-dissipative systems will be represented either by a $|<|V|>|^2$ that continues to have a singularity even in the limit or by states that, in the limit, bunch into one or more localized gorups (at points in energy space) leading to a singular $f(\omega)$. The results of such properties could be persistent correlations or oscillations that survive even in the thermodynamic limit. Examples of such behaviour have been met with in the last of refs. [19].

I should point out that the details in the above argument are not particularly new. What is new (to the best of my knowledge) is the idea of looking at $W(t)$ as a Fourier transform and of connecting thereby the dissipative properties of $W(t)$ to system properties $|<|V|>|^2$ and $f(\omega)$. An advantage of this viewpoint is that points (i)-(iv) are incorporated in a simple way; a serious disadvantage is the cavalier disregard of such issues as the (diagonal) singular properties of V and the effects (for instance secular terms and divergences) of truncating the exact expression of $W(t)$.

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