Exact solution of the stochastic Liouville equation and application to an evaluation of the neutron scattering function

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The evolution equation for the density matrix of a moving particle in a crystal is reformulated as one presenting a (formal) trapping problem and an exact solution obtained with the help of the Montroll defect technique. The solution is used to calculate the neutron scattering function. An explicit evaluation is carried out for a particle moving along a linear chain via nearest-neighbor interactions and the temperature dependence of the line shape is studied exactly as well as in limits.

I. INTRODUCTION

This paper has two purposes: (i) to present a new method for the exact solution of a density-matrix evolution equation used frequently in modern transport theory, and (ii) to evaluate, with the help of that solution, a specific observable, viz., the neutron scattering function. The transport equation is the stochastic Liouville equation (SLE).[1–5] It has recently found extensive use in various fields of physics. The method of solution we present is based on the "defect" technique[6] developed particularly by Montroll and collaborators for problems involving the trapping of moving excitations. Although no trapping occurs in the physics of interest to the present work, we will show that the SLE can be reexpressed as presenting a *formal* trapping problem in a manner analogous to that employed in the theory of mutual annihilation of excitons developed by one of the present authors.[7] The result is an exact solution of the SLE in the Laplace and Fourier domain. The exact solution is particularly appropriate as a starting point for the study of the scattering function relevant to experiments involving probe particles such as neutrons. A field of investigation where such a study is important is that of hydrogen motion in metals where unresolved problems remain in the interpretation of some neutron scattering experiments.[8–10] The particular feature that our solution possesses is the ability to address the degree of transport *coherence* of the moving particle which produces the scattering line shape.

Our paper is structured as follows. In Sec. II we introduce the SLE and present the method of solution. In Sec. III we show that the neutron scattering function is especially amenable to analysis with the help of that solution, give a formal expression for the scattering function, and evaluate it explicitly for a linear chain with nearest-neighbor transport interactions. In Sec. IV we plot and discuss the temperature dependence of the exact expression for the scattering cross section along with its special cases in several limits. Conclusions form Sec. V, and a brief appendix demonstrates a simple extension of our analysis to systems involving SLE's more complex than the one introduced in Sec. II.

II. SLE AND METHOD OF SOLUTION

The stochastic Liouville equation in its simplest form is given by

$$\dot{\rho}_{mn} = -i[H,\rho]_{mn} - \alpha(1-\delta_{mn})\rho_{mn} \tag{2.1}$$

and describes the time evolution of the density matrix ρ of the moving particle in the representation of site states m,n. The system in which the particle moves is a crystal, i.e., possesses translational periodicity. The intersite interaction is H. The last term in (2.1) describes the randomizing process whereby the off-diagonal elements of ρ decay, α being the rate at which this process occurs. Alternatively, α may be looked upon as the average rate of scattering among the band states of the particle. In the limit of no scattering, (2.1) describes wavelike or coherent motion whereas, in the opposite limit, it describes hopping or incoherent motion. The indices m,n are vectors in the appropriate number of dimensions. A different form of the SLE is

$$\dot{\rho}_{mn} = -i[H,\rho] - \alpha(1-\delta_{mn})_{\rho_{mn}} + 2\delta_{mn}\sum_r(\gamma_{mr}\rho_{rr} - \gamma_{rm}\rho_{mm}) \tag{2.2}$$

and describes, in addition to the processes included in (2.1), a transport channel wherein the particle hops from sites r to sites m at rates $2\gamma_{mr}$. We shall show the method of solution for (2.1) in the body of the paper and the extension to (2.2) in the Appendix.

The SLE (2.1) can be looked upon as presenting a formal trapping problem in a $2d$-dimensional space, where d is the dimensionality of the system under analysis. We shall use η to denote the "homogeneous" solution of (2.1), i.e., its solution in the absence of the last term,

$$\eta_{mn}(t) = \sum_{m'n'} \psi_{m-m',n-n'}(t)\rho_{m'n'}(0) \ . \tag{2.3}$$

The quantities ψ are the density-matrix propagators, i.e., the solutions of (2.1) for $\alpha=0$ for the initial conditions $\rho_{mn}(0)=\delta_{m0}\delta_{n0}$. If we recast (2.1) as

$$\dot{\rho}_{mn} + \alpha\rho_{mn} = -i[H,\rho]_{mn} + \alpha\delta_{mn}\rho_{mn} \ , \tag{2.4}$$

we see that α produces two perturbations on (2.3): that caused by $\alpha\rho_{mn}$ on the left side and that caused by $\alpha\delta_{mn}\rho_{mm}$ on the right side. In the context of the dynamics of a hypothetical walker whose unperturbed motion is given by (2.3), these two terms represent, respectively, an overall decay akin to the radiative decay of a moving exciton[3] and a trapping or annihilation process[3,7] which takes

place only when $m=n$, i.e., in a special trap-influenced region in the m,n space. The first of the two terms introduces a simple multiplicative factor into the solutions (2.3), but the second requires an analysis through the defect technique.[6] Equation (2.4) takes the form

$$\tilde{\rho}_{mn}(\epsilon)=\tilde{\eta}_{mn}(\epsilon+\alpha)+\alpha\sum_{m'}\tilde{\psi}_{m-m',n-m'}(\epsilon+\alpha)\tilde{\rho}_{m'm'}(\epsilon) \tag{2.5}$$

in the Laplace domain, where ϵ is the Laplace variable and tildes denote Laplace transforms. The case $m=n$ gives

$$\tilde{\rho}_{mm}(\epsilon)=\tilde{\eta}_{mm}(\epsilon+\alpha)+\alpha\sum_{m'}\tilde{\psi}_{m-m',m-m'}(\epsilon+\alpha)\tilde{\rho}_{m'm'}(\epsilon)\ , \tag{2.6}$$

which involves only diagonal elements of the density matrix in the representation of m,n. We solve (2.6) through the use of discrete Fourier transforms. These are defined through relations such as

$$\rho^k=\sum_m \rho_{mm}e^{ikm}\ , \tag{2.7}$$

where k is generally a vector and km a dot product. The result is

$$\tilde{\rho}^k(\epsilon)=\frac{\tilde{\eta}^k(\epsilon+\alpha)}{1-\alpha\tilde{\psi}^k(\epsilon+\alpha)}\ . \tag{2.8}$$

Equation (2.8) is one of the central results of this paper.

It is straightforward to substitute (2.8) in (2.5). One then finds that the solution of the SLE (2.1) is given by (2.3) with the replacement

$$\tilde{\psi}_{m-m',n-n'}(\epsilon)\rightarrow\tilde{\psi}_{m-m',n-n'}(\epsilon)+\frac{\alpha}{N}\sum_{r,s,k}\left[\frac{e^{ik(s-r)}}{1-\alpha\tilde{\psi}^k(\epsilon+\alpha)}\right]\tilde{\psi}_{m-r,n-r}(\epsilon+\alpha)\tilde{\psi}_{s-m',s-n'}(\epsilon+\alpha)\ . \tag{2.9}$$

This result is exact and explicit. It is explicit in the sense that once one knows the ψ's, i.e., the propagators of (2.1) or (2.4) in the absence of α, one can write down the solutions of (2.1) by following the prescription of (2.9) and the right-hand side of (2.3), for arbitrary initial conditions. The practical usefulness of (2.9) depends on the simplicity, or lack thereof, of the quadrature problem involved in the inversions of the transforms. The result we wish to stress in this paper is (2.8) rather than the general solution (2.9). Indeed, we show below that (2.8) gives us a direct and practical method of evaluating the scattering function.

III. SCATTERING FUNCTION AND ITS EVALUATION FOR A LINEAR CHAIN

The motion of a particle moving among the sites of a crystal, such as a hydrogen atom in a metal, can be studied experimentally by scattering a beam of probe particles that interact weakly with the moving particle. The relevant scattering function $S(k,\omega)$ as derived by Van Hove[11] is conveniently expressed as the Fourier transform in time of a correlation function $I(k,t)$, often called the intermediate scattering function[10,12]

$$I(k,t)=\mathrm{Tr}\rho e^{-ikx}e^{ikx(t)}\ , \tag{3.1}$$

where ρ is the density operator of the target system, i.e., the particle moving in the crystal, k is the momentum transfer, and x is the position operator. The experimental signal is made up of contributions from both the moving particle and the lattice constituents. Under favorable conditions, such as those which commonly prevail for hydrogen in transition metals, the two parts of the signal can be separated from one another. We address only the contribution of the moving particle here. Accordingly, we take x in (3.1) to be the position operator of the moving particle. If the target system is initially in equilibrium, the appropriate form of ρ is canonical. At infinite temperatures, when ρ is proportional to the unit operator, the correlation function $I(k,t)$ becomes simply the Fourier transform of a conditional probability in the basis of the site states of the particle,

$$I(k,t)=\sum_m e^{ikm}P(m,t)=P^k(t)\ . \tag{3.2}$$

Here, and throughout this paper, Debye-Waller factors are neglected for convenience. In obtaining (3.2), the trace in (3.1) is partitioned into a trace over the particle coordinates as seen in (3.2) and a trace over all other coordinates, these constituting a bath. The probability $P(m,t)$ is thus a reduced probability. The variety of methods which may be used to obtain such probabilities has made (3.2) a standard feature of scattering calculations in high-temperature systems.[8,10,12–15]

The infinite-temperature limit assumed in (3.2) is appropriate when k_BT, the product of the Boltzmann constant and the temperature, is much larger than the effective bandwidth of the moving particle. Equation (3.2) can become inadequate at lower temperatures when the symmetry of the observed scattering line shape is affected perceptibly. Under these conditions the departure of the thermal density matrix from the unit matrix must be taken seriously in calculating $I(k,t)$. By transferring the time dependence of $\exp[ikx(t)]$ in (3.1) to the other operators under the trace

$$I(k,t)=\mathrm{Tr}e^{ikx}(e^{-iLt}\rho e^{-ikx})\ , \tag{3.3}$$

wherein L is defined by $LO=[H,O]$ for any operator O, and by defining

$$\rho'(t)=\mathrm{Tr}_{\mathrm{bath}}e^{-iLt}\rho e^{-ikx}\ , \tag{3.4}$$

$$p(m,t)=\langle m\,|\,\rho'(t)\,|\,m\rangle\ , \tag{3.5}$$

we find the finite-temperature generalization of (3.2) to be

$$I(k,t)=\sum_m e^{ikm}p(m,t)=p^k(t)\ . \tag{3.6}$$

While $p(m,t)$ is generally complex, and therefore not a

probability, it behaves like one dynamically: It is a diagonal element of an operator obeying a reduced Liouville–von Neuman equation for a specific, although nonstandard, initial condition. As such, the results of Sec. II may be directly applied to calculate scattering line shapes through the prescription

$$S(k,\omega)=\frac{1}{\pi}\mathrm{Re}\left[\tilde{p}^{\,k}(\epsilon)\Big|_{\epsilon=i\omega}\right]=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}I(k,t)\ . \tag{3.7}$$

We note in passing that (3.6), which gives an observable of interest in terms of the Fourier component of a complex "quasiprobability," is very similar to a result obtained elsewhere[16] which expresses another observable of interest, the conductivity, in terms of the moments of the quasiprobability.

The usefulness of the exact solution of the SLE presented in Sec. II should be completely clear from (3.7). The latter gives the scattering function as the Fourier transform (in time and space) of the site-diagonal elements of an operator which can be taken to follow the evolution dictated by the SLE. Equation (2.8), on the other hand, gives that double Fourier transform explicitly since the passage from a Laplace transform to a one-sided Fourier transform is trivial. The rest of this paper exploits the conjunction of (3.7) and (2.8).

For later use we state here an alternate form of (3.7) which involves a symmetrized form of the correlation function $I(k,t)$ and is similar to one in which the Kubo linear response of the frequency-dependent conductivity is usually displayed:[17]

$$S(k,\omega)=e^{\beta\omega/2}\mathrm{sech}(\tfrac{1}{2}\beta\omega)\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,I^{s}(k,t) \tag{3.8}$$

with the notation $I^{s}(k,t)=\frac{1}{2}[I(k,t)+I(-k,-t)]$, and $\beta=(k_BT)^{-1}$.

As an illustration of (3.7) and (3.8) we calculate $S(k,\omega)$ for a discrete linear chain with the nearest-neighbor transport interaction $H_{mn}=V(\delta_{mn+1}+\delta_{mn-1})$. This requires that $\tilde{\psi}^{\,k}(\epsilon+\alpha)$ and $\tilde{\eta}^{\,k}(\epsilon+\alpha)$ be evaluated, and $S(k,\omega)$ extracted from (2.8) and (3.7). The specific form of the SLE is now

$$\dot{\rho}_{mn}=-iV(\rho_{m-1,n}+\rho_{m+1,n}-\rho_{m,n-1}-\rho_{m,n+1})-\alpha(1-\delta_{mn})\rho_{mn}\ , \tag{3.9}$$

the indices m,n being integers from $-\infty$ to ∞. The solution of (3.9) in the absence of α is well known, the result for the propagators being

$$\psi_{mn}(t)=i^{(n-m)}J_m(2Vt)J_n(2Vt)\ , \tag{3.10}$$

where J_m is the Bessel function of the first kind of order m. The calculation of η^k in (2.8) proceeds as follows: Letting Z denote the partition function, we find in the time domain

$$\eta^{k}(t)=Z^{-1}\sum_{m,r,s}(e^{-iHt})_{mr}(e^{-\beta H}e^{-ikx})_{rs}(e^{iHt})_{sm}e^{ikm}\ . \tag{3.11}$$

This form is exact and independent of the details of the Hamiltonian. Using the result that for our Hamiltonian $[\exp(-iHt)]_{mr}=i^{(r-m)}J_{m-r}(2Vt)$, one obtains

$$\eta^{k}(t)=I_0(2V\beta)^{-1}\sum_{m,n}J_{m+n}(2Vt)J_n(2Vt)I_m(2V\beta)e^{ikm}\ , \tag{3.12}$$

where I_m is the modified Bessel function of the first kind of order m. This may be summed exactly using standard summation formulas[18] to yield

$$\eta^{k}(t)=I_0(2V\beta)^{-1}J_0(4V\sin(\tfrac{1}{2}k)\{(t-\tfrac{1}{2}i\beta)^2-[\tfrac{1}{2}\beta\cot(\tfrac{1}{2}k)]^2\}^{1/2})\ . \tag{3.13}$$

In order to use (2.8) for the line shape calculation, we require the Laplace transforms of the quantities $\psi(t)$ and $\eta(t)$ in (3.10) and (3.13). The former is obtained immediately:[3]

$$\tilde{\psi}^{\,k}(\epsilon+\alpha)=1/[(\epsilon+\alpha)^2+16V^2\sin^2(\tfrac{1}{2}k)]^{1/2}\ . \tag{3.14}$$

The transform of (3.13) can be evaluated in the form of an infinite series

$$\tilde{\eta}^{\,k}(\epsilon+\alpha)=\frac{1}{I_0(2V\beta)}\sum_{l=-\infty}^{\infty}\frac{\zeta_l\{[(\epsilon+\alpha)^2+V(k)^2]^{1/2}-(\epsilon+\alpha)\}^{|l|}}{v(k)^{|l|}[(\epsilon+\alpha)^2+V(k)^2]^{1/2}}I_l(2V\beta)e^{ikl/2} \tag{3.15}$$

where, for convenience, we have defined $V(k)=4V\sin(\frac{1}{2}k)$ and $\zeta_l=\mathrm{sgn}(l)^l$. For practical computations one may either use (3.15) or a numerical evaluation of the Laplace transform of (3.13). We have found it convenient to use the latter procedure.[19] The substitution of that result and of (3.14) in (2.8) gives the scattering function explicitly through either (3.7) or (3.8). We present the results below.

IV. PLOTS AND DISCUSSION

The special contribution of our present calculation of scattering line shapes is that it treats systems with an arbitrary degree of transport coherence. To show this explicitly we present Fig. 1, in which we isolate the effects of coherence from those of temperature by considering the *infinite*-temperature case. In this limit, the present results are equivalent to those of Ref. 5. We have scaled all parameters by $V(k)$. So scaled, the representation of $S(k,\omega)$ in Fig. 1 is independent of momentum transfer and the particle energy bandwidth, i.e., there is no hidden dependence on these quantities.

The narrowing and resurgence of the scattering line seen with increasing $\alpha/V(k)$ is a dynamical consequence of limited quantum-mechanical phase memory. For large

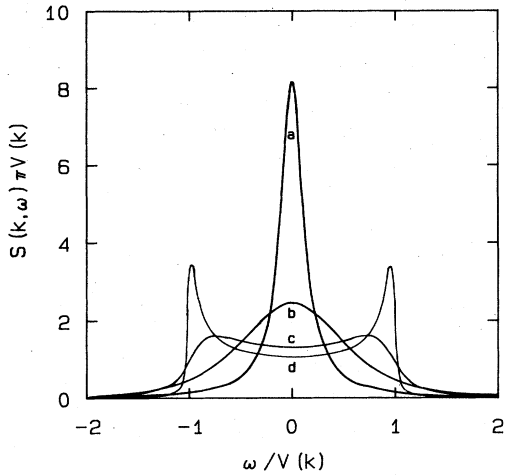

FIG. 1. Neutron scattering line shapes showing the effect of intermediate transport coherence. For small values of the ratio $\alpha/V(k)$, which measures the degree of incoherence, the coherent line is broadened. Detail of the coherent line shape is lost for large values of $\alpha/V(k)$ as the line narrows toward its asymptotically Lorentzian form. Parameter values: Curve *a*, $\alpha/V(k)=4.0$; curve *b*, $\alpha/V(k)=1.0$; curve *c*, $\alpha/V(k)=0.25$; curve *d*, $\alpha/V(k)=0.025$. For all curves $k_BT=\infty$, and k is arbitrary.

values of this parameter, our results tend toward those of the Markoffian limit of (2.1), which is a simple master equation with nearest-neighbor hopping rates $2V^2/\alpha$. The limiting form of the scattering function is a Lorentzian with a width function $2V(k)^2/\alpha$, which decreases as $\alpha/V(k)$ increases. Our line shape is thus seen to be asymptotically identical to the usual one for diffusing particles. Needless to say, this equivalence is only asymptotic: For finite values of $\alpha/V(k)$ the detail of the line shape incorporates the degree of coherence in the transport as well as the rate of macroscopic motion.

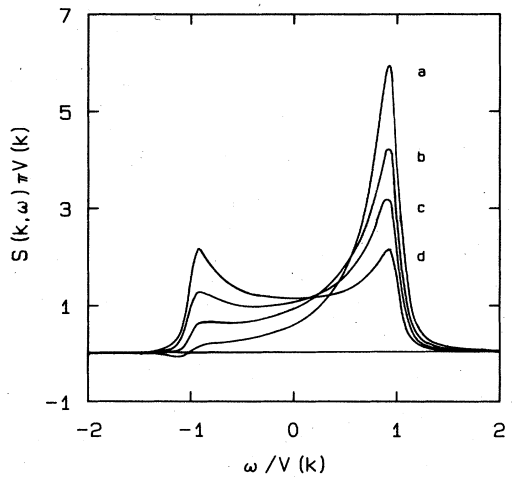

FIG. 2. Scattering function calculated directly from (2.1) and (3.7) for various temperatures. See text for discussion. Parameter values: curve *a*, $k_BT=V$; curve *b*, $k_BT=2V$; curve *c*, $k_BT=4V$; curve *d*, $k_BT=\infty$. For all curves, $\alpha/V(k)=0.1$, $ka=\pi$.

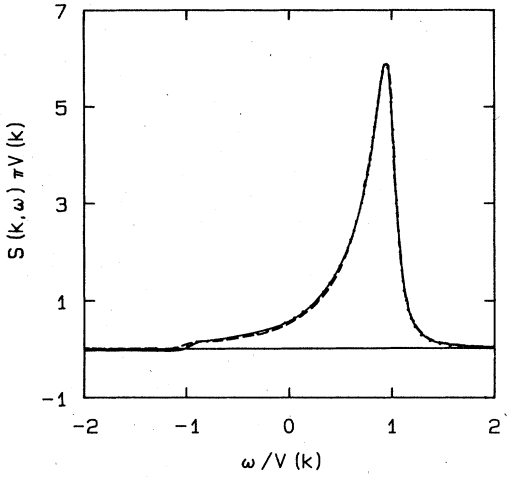

FIG. 3. Comparison of $S(k,\omega)$ (——), $S^s(k,\omega)$ (· · · ·), and $S^a(k,\omega)$ (— — —) for $k_BT=V$, $\alpha/V(k)=0.1$, $ka=\pi$. Both $S^s(k,\omega)$ and $S^a(k,\omega)$ possess the proper symmetries and are positive definite. The integrated intensities of $S^s(k,\omega)$ and $S(k,\omega)$ are each equal to the infinite temperature value, as required by the condition that $I(k,0)$ is independent of temperature.

At finite temperature we expect to see a shift of intensity to the energy-loss (positive ω) side of the line, reflecting the detailed balance properties inherent in equilibrium transition rates.[20] Indeed, such intensity shifting is seen in SLE-derived line shapes (Figs. 2—6). However, when the results are pushed to sufficiently low temperatures, one sees (e.g., from the negativities in Fig. 2) that the intensities calculated directly from (3.7) fail to satisfy the relationship

$$S(k,\omega)=e^{-\beta\omega}S(-k,-\omega)\ , \tag{4.1}$$

expected to hold point by point across the line (Fig. 2). The failure of such "direct" line shape calculations to

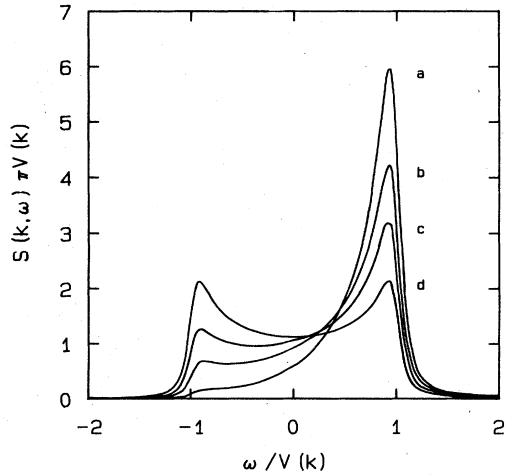

FIG. 4. Scattering function of Fig. 2 after the application of the symmetrization prescription (4.3). Parameter values: curve *a*, $k_BT=V$; curve *b*, $k_BT=2V$; curve *c*, $k_BT=4V$; curve *d*, $k_BT=\infty$. For all curves $\alpha/V(k)=0.1$, $ka=\pi$.

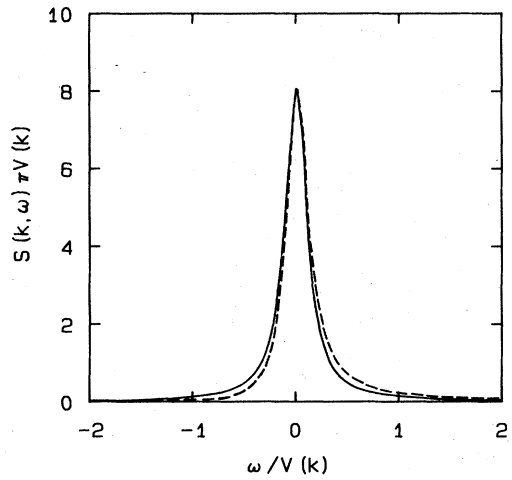

FIG. 5. Scattering function for highly incoherent transport after the symmetrization prescription (4.3). Parameter values: – – –, $k_BT=4V$; ——, $k_BT=\infty$. For each curve $\alpha/V(k)=4.0$, $ka=\pi$.

maintain the detailed balance symmetry at finite temperatures is due to the approximate nature of the transport description. Indeed, this is normal in the traditional application of the classical prescription (3.2), which only yields line shapes even in frequency. Such line shapes can be valid only at infinite temperatures, and it is common practice to "improve" them with a correction factor $\exp(\beta\omega/2)$

$$S(k,\omega)=e^{\beta\omega/2}S_0(k,\omega)\ , \tag{4.2}$$

where $S_0(k,\omega)$ is the even line shape derived from (3.2).[12] Unlike the classical treatments, the result of (2.1) and (3.7) is a line shape which is of indefinite symmetry. In restoring the detailed balance properties which the line shape must possess on general grounds, we wish to utilize the fact that SLE-derived line shapes are already "improved" in the sense that they are quite well balanced if temperatures are not too low. We note that the detailed balance relation may be written equivalently as

$$S(k,\omega)=\frac{e^{\beta\omega/2}}{2\cosh(\frac{1}{2}\beta\omega)}[S(k,\omega)+S(-k,-\omega)]\ . \tag{4.3}$$

If (4.1) is satisfied by a candidate line shape function $S(k,\omega)$, then (4.3) is also satisfied and merely shows how $S(k,\omega)$ may be expressed in terms of its symmetric part. On the other hand, if (as in the present case) the derived function $S(k,\omega)$ fails to satisfy (4.1), then (4.3) fails as well. The right-hand side of (4.3) may then be used to define a new function $S^s(k,\omega)$ which satisfies (4.1) *exactly*. Figure 3 compares an $S^s(k,\omega)$ and the $S(k,\omega)$ from Fig. 2 used to generate it. One sees explicitly that $S^s(k,\omega)$ does not possess the problems shown by $S(k,\omega)$, but is otherwise practically identical to $S(k,\omega)$.

Alternatively, one could define a function $S^a(k,\omega)$ formed from the antisymmetric part of $S(k,\omega)$,

$$S^a(k,\omega)=\frac{e^{\beta\omega/2}}{2\sinh(\frac{1}{2}\beta\omega)}[S(k,\omega)-S(-k,-\omega)]\ ,$$

and use it to address the detailed balance problem in a similar manner. In fact, Fig. 3 shows explicitly that there is almost no quantitative difference between $S^a(k,\omega)$ and $S^s(k,\omega)$. Therefore, we will consider only $S^s(k,\omega)$ in the rest of the paper. We note also that (i) for inversion-symmetric systems such as we consider here, the integrated intensities of $S^s(k,\omega)$ and $S(k,\omega)$ for a given k are identical and conserved against variations in parameters, and (ii) the small $-\omega$ behaviors of $S^s(k,\omega)$ and $S(k,\omega)$ are the same.

Our prescription for the calculation of scattering line shapes therefore consists of the derivation of $S(k,\omega)$ from (3.7) and the substitution of this approximate result into (4.3). The final line shape is $S^s(k,\omega)$. We stress that this procedure is entirely equivalent to using the relation (3.8) following the calculation of the symmetrized correlation function $I^s(k,t)$ from the SLE.

Figures 4 and 5 present typical results of the SLE as improved by the symmetrization prescription (4.3). In Fig. 4 a fairly high degree of transport coherence is considered over a range of temperatures, while in Fig. 5 a low-coherence result is shown. While high-coherence results provide more detailed information about the system, it is the low-coherence case which is most commonly encountered in experiments probing atomic transport in extended systems.

Results presented thus far have been exact consequences of the stochastic Liouville equation. Also of interest are approximate results, accurate to low order in some relevant parameter. We will now explicitly consider the full quantity $\tilde{\rho}^k(\epsilon)$, and from it produce approximate $S(k,\omega)$ using (3.7). From such $S(k,\omega)$, $S^s(k,\omega)$ will be obtained by applying (4.3) without further approximation.

Combining (2.8), (3.14), and (3.15) one obtains

$$\tilde{\rho}^k(\epsilon)=\sum_{l=-\infty}^{\infty}\frac{\zeta_l\{[(\epsilon+\alpha)^2+V(k)^2]^{1/2}-(\epsilon+\alpha)\}^{|l|}}{V(k)^{|l|}\{[(\epsilon+\alpha)^2+V(k)^2]^{1/2}-\alpha\}}\frac{I_l(2V\beta)}{I_0(2V\beta)}e^{ikl/2}\ . \tag{4.4}$$

Retaining only terms of lowest order in βV, the infinite-temperature result is modified to yield

$$S(k,\omega)\approx\frac{1}{\pi}\frac{R(\omega)\cos[\Theta(\omega)](1+\frac{1}{2}\beta\omega)}{R(\omega)^2-2\alpha R(\omega)\cos[\Theta(\omega)]+\alpha^2} \tag{4.5a}$$

with the auxiliary definitions

$$R(\omega)=\{[\alpha^2+V(k)^2-\omega^2]^2+4\omega^2\alpha^2\}^{1/2}\ , \tag{4.5b}$$

$$\Theta(\omega)=\arg\{[(i\omega+\alpha)^2+V(k)^2]^{1/2}\}\ . \tag{4.5c}$$

We note that this result, which is first order in βV, satisfies (4.1) to second order in $\beta\omega$. Since the first-order term is odd in frequency, the correction is lost when (4.3) is applied. The result is

$$S^s(k,\omega)\approx\frac{1}{\pi}\frac{e^{\beta\omega/2}}{\cosh(\frac{1}{2}\beta\omega)}\frac{R(\omega)\cos[\Theta(\omega)]}{R(\omega)^2-2\alpha R(\omega)\cos[\Theta(\omega)]+\alpha^2}\ . \tag{4.6}$$

To this low order, the structured part of the line shape is independent of temperature and identical to the infinite-temperature line shape. The next correction, obtained by retaining terms to second order in βV, contributes to $S^s(k,\omega)$ with the result

$$S^s(k,\omega)\approx\frac{1}{\pi}\frac{e^{\beta\omega/2}}{\cosh(\frac{1}{2}\beta\omega)}\left\{\frac{R(\omega)\cos[\Theta(\omega)]}{R(\omega)^2-2\alpha R(\omega)\cos[\Theta(\omega)]+\alpha^2}+\frac{\{R(\omega)\cos[\Theta(\omega)]-\alpha\}\{R(\omega)^2-2\alpha R(\omega)\cos[\Theta(\omega)]+\alpha^2-\omega^2\}}{R(\omega)^2-2\alpha R(\omega)\cos[\Theta(\omega)]+\alpha^2}\left[\frac{2V\beta\cos(k)}{4V\sin(\frac{1}{2}k)}\right]\right\}\ . \tag{4.7}$$

While the above approximations are restricted in the temperature range over which they apply, they are valid for arbitrary frequency, momentum transfer, and degree of coherence. To find approximate forms valid at lower temperatures, an alternative parameter is needed. A useful smallness parameter is $V(k)/(\epsilon+\alpha)$. Formulas developed in powers of $V(k)/(\epsilon+\alpha)$ will display the important features of the line shape in the incoherent regime ($\alpha\gg V$), the small-momentum-transfer regime [$k\ll|(i\omega+\alpha)/2V|$], and in the wings [$\omega\gg V(k)$]. Expanding the radicals in (4.4) and retaining terms to first order in $V(k)/(\epsilon+\alpha)$ yields

$$\tilde{\rho}^k(\epsilon)\approx\frac{1+i[V(k)/(\epsilon+\alpha)]I_1(2V\beta)\sin(\frac{1}{2}k)}{\{\epsilon+\frac{1}{2}[V(k)^2/(\epsilon+\alpha)]\}I_0(2V\beta)}\ . \tag{4.8}$$

Applying (3.7) yields the direct line shape

$$S(k,\omega)\approx\frac{1}{\pi}\frac{\frac{1}{2}\alpha V(k)^2\left[1+\frac{\omega}{2V}\frac{I_1(2V\beta)}{I_0(2V\beta)}\right]}{[\frac{1}{2}V(k)^2-\omega^2]^2+\omega^2\alpha^2} \tag{4.9}$$

and applying the symmetrization prescription (4.3) to (4.9) yields the properly balanced line

$$S^s(k,\omega)\approx\frac{1}{\pi}\frac{e^{\beta\omega/2}}{\cosh(\frac{1}{2}\beta\omega)}\frac{\frac{1}{2}\alpha V(k)^2}{[\frac{1}{2}V(k)^2-\omega^2]^2+\omega^2\alpha^2}\ . \tag{4.10}$$

The temperature-independent factor in (4.10) is, interestingly, just the familiar stochastically broadened line shape due to Kubo[21] for a two-state system with energy levels at $\pm V(k)/\sqrt{2}$.

Finally, it is easily seen from (4.10) that when α is large in comparison to both ω and $V(k)$, the well-known diffusion result is recovered:

$$S^s(k,\omega)\approx\frac{1}{\pi}\frac{e^{\beta\omega/2}}{\cosh(\frac{1}{2}\beta\omega)}\frac{\left[\frac{V(k)^2}{2\alpha}\right]}{\omega^2+\left[\frac{V(k)^2}{2\alpha}\right]^2}\ . \tag{4.11}$$

V. CONCLUSION

The contributions of the present work are three: (i) the defect-technique method of solution of the stochastic Liouville equation with (2.8) and (2.9) as the end result, (ii) the application of this result, particularly (2.8), for the exact calculation of the scattering line shape in a representative one-dimensional system, as in (3.8)—(3.15), and (iii) a resolution of the detailed balance problem characteristic of the stochastic Liouville equation as explained in the discussion following (4.3). We comment on each of these in turn.

The stochastic Liouville equation has been derived and explored in numerous ways in diverse contexts.[4,22–24] The characteristic feature of the new method of solution we have presented is that it is based on recasting the equation as describing a formal trapping or annihilation problem, although such capture processes do not occur in the physics under consideration. The correspondence between the method of solution given here and the annihilation analysis of Ref. 7 may be understood through an inspection of (2.4). The purely coherent evolution, i.e., the case of no bath interactions, is taken to correspond to the annihilationless system. The effects of the bath are looked upon as producing decays: through an overall depletion at the rate α as well as through a formal "capture" process occurring in a restricted region of the space under consideration. The restricted region is "along the diagonal" in the site representation of the density matrix and corresponds to the destruction region that appears in the annihilation problem.[7] The space under analysis has twice the number of dimensions as the physical crystal in both cases: in the annihilation problem because the particles annihilate in pairs, and in the present problem because the evolving object is a density matrix—rather than a probability or an amplitude—and therefore a double-indexed quantity. Exact solution of trapping problems is practical only when the defect region is small in extent.[6] Although the defect region for the present problem is initially infinite in extent, we are successful in reducing its size through the use of the Fourier transform. This is identical to the annihilation case and it is the translationally invariant na-

ture of the system under consideration that makes the reduction possible. The final solution for the annihilation problem is presented[7] in the Laplace-Fourier domain as the product of a correction factor and the ϵ-displaced ($\epsilon \rightarrow \epsilon + \alpha$) solutions for the pure crystal without annihilation. The final solution for the stochastic Liouville equation appears here in the Laplace-Fourier domain as the product of a correction factor and the ϵ-displaced solutions for the purely *coherent* crystal. In the simple one-dimensional model with nearest-neighbor transport interactions which we have used to illustrate our method, the purely coherent solutions are known explicitly in terms of Bessel functions. All the required information about the full solution of the stochastic Liouville equation, in particular the scattering line shape, is therefore obtained easily through the use of our method.

Our interest in the present paper is in applications of the stochastic Liouville equation to light interstitial transport and we note that a form of the equation has appeared in the metal hydride literature.[4] Its primary use has been to extract diffusion constants for specific transport models. A limiting case of the SLE is the master equation, which describes completely incoherent motion of interstitials and has long been used as the basis of neutron spectroscopic studies of jump diffusion.[13] It is in part the apparent inability of such theories to explain a growing body of neutron spectroscopic data[8–10] that has motivated investigation into alternative transport models. As Figs. 1–5 show, our analysis allows us to study the effects of arbitrary coherence and finite temperature in full detail.

The stochastic Liouville equation possesses an undesirable characteristic which is well known. The assumption of a universal rate α for the decay of ρ_{mn} forces the SLE to produce equilibrium solutions which do not possess the correct thermal behavior: All off-diagonal elements of the density matrix in the site representation vanish in equilibrium, and all k states are occupied with equal probability. This result is obviously incorrect unless the temperature is infinite. It is expected that the scattering function would be affected by this failing of the SLE, since, on balance, line shape symmetry is dependent on the detail of the equilibration process. This shortcoming of the SLE has been recognized in the exciton literature and at least two attempts have been made to correct it.[25,26] In one of them[25] a form of the SLE has been constructed specifically to build into the equation the correct equilibrium solution. While such a procedure is simple for the dimer considered in Ref. 25, the large number of k states (or of ρ_{mn}) involved in crystal makes the generalization of that procedure for our present purpose impractical. Moreover, that remedy is unable to address the failure of directly calculated line shapes to meet detailed balance criteria. The approach we have taken in the present paper consists of calculating from the SLE a symmetrized correlation function rather than the simple $I(k,t)$, and using the general relation, viz. (3.8), to connect it to the scattering function. The general relation is valid independently of the dynamics or the approximation inherent in the SLE. On the other hand, the symmetrized correlation function calculated from the SLE contains the specific dynamics particular to the latter. By using our method, one thus obtains a scattering function that contains the precise dynamics of the SLE as well as the correct detailed balance properties. It is perhaps worth emphasizing that, as far as the scattering line shape is concerned, the detailed balance problem does not even arise if one uses our prescription from the very beginning of the analysis. It is further important to observe that the departure from the detailed balance relationship inherent in the direct consequence of the SLE is, perhaps surprisingly, quite small even at low temperatures, as Fig. 2 shows explicitly.

Some generalizations of the theory of neutron scattering incorporating the interplay of hopping and tunneling motion of interstitial atoms have been proposed.[15] The present formulation of the neutron scattering function is formally distinguished from others in that it is applicable at finite temperatures and is derived from a reduced density-matrix equation. When the evolution equation is the stochastic Liouville equation, as in our exemplary calculations, the expected broadening of the line shape with increasing incoherence is seen to result ultimately in the narrowing of the line. We note that the narrowing behavior is a consequence of diminishing transport coherence and cannot be reproduced by convoluting the coherent line shape with a broadening distribution as in Ref. 15. Moreover, while a hopping channel may be incorporated into the SLE as in (2.2) and in the Appendix, the broadening of scattering line shapes exhibited in this paper is not attributable to the hopping of the probed particle. We have carried out a study of the consequences of the interplay of band and hopping transport by our method, and the details are being reported elsewhere.[27]

In all the expressions and figures presented in this paper the quantity $\alpha/V(k)$ plays the role of the incoherence parameter: Its magnitude depends directly on the relative magnitude of the bath interactions and the intersite transfer interaction. For fixed momentum transfer k/a this quantity is proportional to α/V, which clearly measures the reciprocal of the mean free path of the moving particle in units of the lattice constant. This is evident from the fact that, with a as the lattice constant, $\sqrt{2}Va$ is the average group velocity and $1/\alpha$ is the average time between collisions (bath interaction events). What is particularly interesting in the present problem is the role played by the entire expression $\alpha/V(k)$ rather than by α/V. For small values of momentum transfer, $\sin(\frac{1}{2}k)$ may be replaced by $\frac{1}{2}k$. The parameter $\alpha/V(k)$ is proportional to the ratio of the characteristic length of the neutron scattering probe, viz., a/k, to the coherence length of the atomic motion, viz., the mean free path. Whether coherence features will manifest themselves in the scattering line shape will depend on the magnitude of this ratio. We present Fig. 6 to clarify this point and note that, to the extent that momentum transfer may be varied in an experiment, it may be possible to undo the Markoffian limit sufficiently to determine the intrinsic ratio α/V. In Fig. 6, α/V is constant, but the transition from coherent to incoherent behavior is produced by the variation in the amount of momentum transfer. In the completely incoherent situation, i.e., when the standard diffusion result (4.11) applies, the relevant ratio is that of a/k to $[(V^2/\alpha)a^2/\omega]^{1/2}$. The significance of the latter quantity

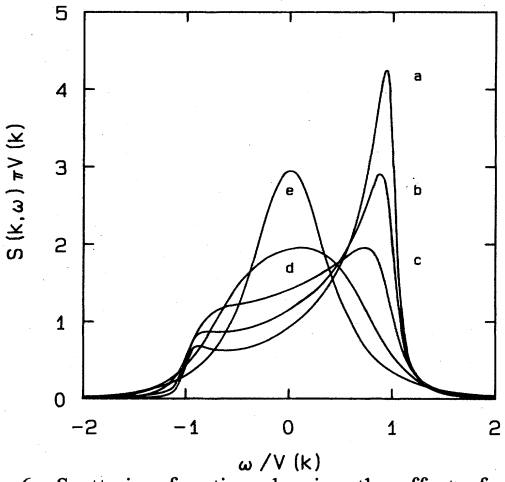

FIG. 6. Scattering function showing the effect of varying momentum transfer. Transport has been taken to be intrinsically highly coherent, and the symmetrization prescription (4.3) has been applied. Parameter values: curve a, $ka=\pi$; curve b, $ka=\pi/2$; curve c, $ka=\pi/4$; curve d, $ka=\pi/10$; curve e, $ka=\pi/20$. For each curve, $\alpha/V=0.4$, $k_BT=2V$.

is that it is the distance traversed diffusively by the moving atom in a time period $1/\omega$ characteristic of the neutron probe. The diffusion constant is proportional to $(V^2/\alpha)a^2$. The relevant ratio for this incoherent case is therefore again that of the neutron probe length to an atomic motion length. The situation described here is similar to that discussed elsewhere in the context of the measurement of exciton transport and coherence through Ronchi ruling experiments.[28]

The work reported in this paper is exact but restricted in the illustrative example discussed to one-dimensional systems. While the qualitative features of the results should be of value in the context of light interstitial transport, an extension to a three-dimensional system is necessary before direct comparison to experiment can be made. Such work is under way.

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APPENDIX

The purpose of this appendix is to obtain an exact solution of the stochastic Liouville equation and a formula for the scattering function such as (2.8) starting, not from the simple form of the SLE (2.1), but from the form (2.2). On writing the latter as

$$\dot{\rho}_{mn}+\alpha\rho_{mn}=-i[H,\rho]_{mn}+\delta_{mn}\left[\alpha\rho_{mn}+2\sum_r(\gamma_{mr}\rho_{rr}-\gamma_{rm}\rho_{mm})\right], \tag{A1}$$

we find that the defect term is more complex than that encountered in (2.4) for the simpler SLE, but still lies along the region $m=n$. Following standard usage we define the matrix A in terms of the gain-loss matrix γ through the prescription

$$A_{mr}=-\gamma_{mr},\quad m\neq r$$
$$A_{mm}=\sum_r\gamma_{rm}\ .$$

In consequence, the matrix elements $\alpha\delta_{mr}$ in Sec. II are replaced by the quantities $\alpha\delta_{mr}-A_{mr}$, and (2.5) is generalized to yield the solution of (A1)

$$\tilde{\rho}_{mn}(\epsilon)=\tilde{\eta}_{mn}(\epsilon+\alpha)+\sum_{m'}\tilde{\psi}_{m-m',n-m'}(\epsilon+\alpha)\left[\alpha\tilde{\rho}_{m'm'}(\epsilon)+\sum_r A_{m'r}\tilde{\rho}_{rr}(\epsilon)\right]. \tag{A2}$$

The translational invariance of the crystal implies that the A_{mr} are functions of $m-r$ alone and immediately leads to

$$\tilde{\rho}^k(\epsilon)=\frac{\tilde{\eta}^k(\epsilon+\alpha)}{1-(\alpha-A^k)\tilde{\psi}^k(\epsilon+\alpha)} \tag{A3}$$

as the generalization of (2.8) in the text of the paper.

The inclusion of the additional transport channel through the hopping rates A_{mr} leaves the scattering function unchanged except for the replacement of α by $\alpha-A^k$ as the factor multiplying $\tilde{\psi}^k$ in (2.8). It is straightforward to examine line shapes with (A3) instead of (2.8), and we have done so in Ref. 5 for the case of infinite temperature.

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