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PHYSICAL REVIEW A VOLUME 7, NUMBER 3 MARCH 1973

Density Expansion of the Memory Operator in Pressure-Broadening Theory

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(Received 9 August 1972)

The motion of a radiating atom immersed in a gas of other atoms, the bath, may be described by means of a nonunitary time-evolution operator $U(t) = (\mathrm{Tr}_B\rho)^{-1}\,\mathrm{Tr}_B\rho e^{itH^\times}$ acting in its Liouville space (Tr_B is the trace over bath variables, ρ is the density matrix, and $H^\times$ is the quantum-mechanical Liouvillian). In a previous paper, $U(t)$ was written in the form $U(t) = \exp_{\rightarrow}[i\int_0^t dt'\,L_1(t')]$ ($\exp_{\rightarrow}$ denotes a time-ordered exponential), and the time-dependent *effective Liouvillian* $L_1(t)$ was expanded in powers of a "reduced density," or *activity*. In this paper the Fourier transform $U(\omega) = \int_0^\infty dt\, e^{-i\omega t}U(t)$ is written in the form $iU(\omega) = [\omega - L_2(\omega)]^{-1}$, and the frequency-dependent *effective Liouvillian* $L_2(\omega)$, or "memory operator," is expanded in powers of the reduced density. It is argued that in treating $L_2(\omega)$ to first order in the reduced density, one effectively allows the radiator to interact with only one perturber at a time, thus neglecting all multiple-collision effects. This is in contrast to performing the same-order approximation on $L_1(t)$, which is equivalent to treating different perturbers as uncorrelated, but still allows for multiple-collision effects. By adding the terms of higher order in the expansion of $L_2(\omega)$, one allows the radiator to interact simultaneously with two, three,... perturbers.

I. NOTATION

The time variable τ and the frequency ω will be considered conjugate variables in the sense that for any function $f(\tau)$:

$$f(\omega) \equiv \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} f(\tau) \equiv \mathfrak{F}\{f(\tau)\}\,,$$

$$f(\tau) \equiv (2\pi)^{-1} \int_{-\infty}^{\infty} d\omega\, e^{i\omega\tau} f(\omega) \equiv \mathfrak{F}^{\dagger}\{f(\omega)\}\,,$$

where $\mathfrak{F}$ means Fourier transform. Functions of τ are always defined as vanishing on the negative semiaxis, so that

$$f(\omega) = \int_0^\infty d\tau\, e^{-i\omega\tau} f(\tau)\,,$$

and ω will be understood to have a small negative imaginary part whenever it is necessary to assure the convergence of the Fourier integral.

Convolution products are denoted by an asterisk:

$$f(\tau)*g(\tau)\equiv\int_{-\infty}^{\infty}dt\,f(\tau-t)g(t)\ ,$$

$$f(\omega)*g(\omega)\equiv(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega'\,f(\omega-\omega')g(\omega')\ ;$$

we have

$$\mathfrak{F}\{f(\tau)*g(\tau)\}\equiv f(\omega)g(\omega)\ ,$$

$$\mathfrak{F}\{f(\tau)g(\tau)\}\equiv f(\omega)*g(\omega)\ .$$

Given any operator A, the operator $A^\times$ is defined by its action on any operator B:

$$A^\times B=AB-BA\ .$$

Time-ordered exponentials are denoted by $e_{\rightarrow}$ or $\exp_{\rightarrow}$, where the arrow indicates the direction of increase of the time arguments.

II. INTRODUCTION

When considering a system $\mathcal{S}$ in contact with a bath $\mathcal{B}$, such as a radiating atom immersed in a gas, it is convenient to describe its time evolution by means of a non-Hermitian operator $U(\tau)$ acting in the Liouville space of $\mathcal{S}$, and governing its motion under the influence of the bath; the "time-evolution operator" $U(\tau)$ is defined[1]

$$U(\tau)\equiv(\mathrm{Tr}_B\rho)^{-1}\,\mathrm{Tr}_B\rho e^{i\tau H^\times}\ , \tag{2.1}$$

where Tr_B (Tr_s) is the trace over bath (system) variables, ρ is the initial density matrix, and $H^\times$ is the quantum-mechanical Liouvillian, H being the total Hamiltonian. The average value of any system observable, A_s, at time τ is then written

$$\mathrm{Tr}\rho e^{i\tau H}A_s\,e^{-i\tau H}=\mathrm{Tr}_s\sigma U(\tau)A_s\ ,$$

where

$$\sigma\equiv\mathrm{Tr}_B\rho \tag{2.2}$$

is the reduced density matrix describing the state of $\mathcal{S}$ at time zero. Similarly one can express time-correlation functions of $\mathcal{S}$ observables by means of $U(\tau)$ and σ. In the specific case of pressure broadening,[2,3] we require the autocorrelation function of the radiating dipole (or multipole) operator D:

$$I(\tau)=\mathrm{Tr}\rho e^{i\tau H}De^{-i\tau H}D=\mathrm{Tr}_sD\sigma U(\tau)D\ .$$

Due to the very large number of degrees of freedom of the bath, $U(\tau)$ cannot, in general, be calculated exactly; moreover, its perturbation or density expansions do not converge uniformly with respect to τ and consequently, cannot be truncated (the successive terms of the expansions behave asymptotically as increasing powers of τ). One therefore seeks to express $U(\tau)$ in terms of other quantities having expansions which *can* serve as approximation schemes. More precisely, we wish to write $U(\tau)$ as a functional F of some other quantity $L(t)$,

$$U(\tau)=F[L(t)]\ ,$$

where $L(t)=F^{-1}[U(t)]$ possesses expansions

$$L(t)=L^{(0)}+L^{(1)}+L^{(2)}+\dots$$

[$L^{(0)}(t)$ corresponds to the absence of the bath] that *can* be truncated; $U(\tau)$ can then be approximated by keeping only the first few terms in the expansion of $L(t)$, e.g.,

$$U(\tau)\approx F[L^{(0)}(t)+L^{(1)}(t)]\ .$$

The most direct procedure would be to first find a $L(t)=F^{-1}[U(t)]$ having expansions that can be truncated, and then determine the functional form F. There are, however, several different functionals of $U(t)$ satisfying the above requirement, and a specific choice must be dictated by the additional requirement that the expression of U in terms of L be sufficiently simple and practical, and also, preferably, that it be physically meaningful. It is actually more profitable to start from this last requirement and, making use of one's physical intuition, first choose a functional form $F[\ ]$, then verify that $F^{-1}[U(t)]$ has useful expansions. In this way, two approaches suggest themselves naturally when one notices that in the absence of the bath, $U(\tau)=e^{i\tau H_s^\times}$ and $iU(\omega)=(\omega-H_s^\times)^{-1}$, where $H_s^\times$ is the Liouvillian of the unperturbed $\mathcal{S}$.

In the first approach, we write

$$\begin{aligned}U(\tau)&=\exp_{\rightarrow}\Big[i\int_0^\tau dt\,L_1(t)\Big]\ ,\\ iL_1(t)&=U(t)^{-1}\dot{U}(t)\end{aligned} \tag{2.3}$$

($\dot{U}=dU/dt$), and in the second approach, we set

$$\begin{aligned}iU(\omega)&=[\omega-L_2(\omega)]^{-1}\ ,\\ L_2(\omega)&=\omega-[iU(\omega)]^{-1}\ .\end{aligned} \tag{2.4}$$

Thus, in (2.3), we replace the unperturbed Liouvillian $H_s^\times$ of $\mathcal{S}$ by a time-dependent *effective Liouvillian* $L_1(t)$ (and time order since we have operators), and in (2.4), $H_s^\times$ is replaced by a frequency-dependent effective Liouvillian $L_2(\omega)$. Since in the absence of the bath L_1 and L_2 equal $H_s^\times$, we may write

$$L_1(t)=H_s^\times+R(t)\ , \tag{2.5}$$

$$L_2(\omega)=H_s^\times+C(\omega)\ , \tag{2.6}$$

where $R(t)$ and $C(\omega)$ contain the effect of the bath and vanish in its absence. One must deduce the perturbation expansions of R and C from those of U, and verify that they can be approximated by their first or first few terms.

The above procedure was carried out in Ref. 1 for the "exponential" method involving $R(t)$. (*Note added in proof.* See, however, Ref. 22.) In the present paper, we discuss the "resolvent" approach involving $C(\omega)$. The resolvent form (2.4) is usually reached by means of Zwanzig's projection-operator methods,[4,5] and $C(\omega)$ (or related operators) is generally referred to as a *memory operator*, a term suggested by the form of its functional relation to U in the time domain. It seems quite complicated to deduce the density expansion of C from Zwanzig's expressions,[4] while it is obtained quite readily by the more direct procedure outlined above. Still, in order to exhibit clearly the structure of the density expansion, we shall employ methods analogous to Zwanzig's, with use of a special type of projection operator which may be called a "time-overlap destroying" operator.

The preceding considerations stem from mathematical imperatives. From the physical point of view, the question arises as to what is the physical meaning of treating a given $L(t)$ to some order in an expansion parameter, and the related question of what is the physical significance of each term in the expansion. Clearly, to different functions L_1, L_2, ... correspond different answers to these questions.

It was seen in Ref. 1 that by treating $R(t)$ to first order in the reduced density n, one is treating collisions of the radiator with perturbing atoms as *independent* of each other; in other words, the radiator can interact with, or "feel," several perturbers simultaneously, but the perturbers do not feel each other. This approximation may therefore be called an "independent-collision approximation." By including the second-order term in the expansion of $R(t)$, one allows for pairs of correlated perturbers, and so on for higher-order approximations.

In the case of $C(\omega)$, it will be found that by treating it to first order in the reduced density, one is letting the radiator interact with only one perturber at a time: During a multiple collision, not only do the perturbers not feel each other, but also the radiator feels only one perturber at a time, that is, only one of the radiator-perturber interactions is turned on at any instant. This may be called a "nonoverlapping-interactions approximation." By adding terms of higher order in the expansion of $C(\omega)$, we allow the radiator to simultaneously feel two, three, ... perturbers.

The difference between the "independent-collision" and the "nonoverlapping-interactions" approximations reflects itself in the corresponding expressions of the spectrum: The independent-collision spectrum contains features arising from the simultaneous interaction of the radiator with several perturbers, such as the pressure shift of the wing structure, and possibly additional fine structure,[6] features which are absent in the nonoverlapping-interactions spectrum which yields wings given simply by the one-perturber spectrum. Clearly, the independent-collision approximation is better than the nonoverlapping-interactions approximation, the latter actually being a further approximation to the former. On the other hand, the resolvent form (2.4) is simpler and more practical than the ordered-exponential form (2.3).

In Sec. III, the relevant results of Ref. 1 are summarized and expressed using a notation more suitable for the purposes of this paper; also, a (uniformly convergent) density expansion of $U(\omega)$ is given, which allows one to assess the effect of multiple collisions on the spectrum. In Sec. IV, quantities $M(\hat{\omega}) \equiv U(\omega) i\hat{\omega} - 1$ and $N(\hat{\omega}) \equiv (1/\hat{\omega})C(\omega)$, with $\hat{\omega} \equiv \omega - H_s^\times$, are introduced, which have perfectly symmetric mutual relations; $N(\hat{\omega})$ is treated to first order in the reduced density n, and the resulting nonoverlapping-interactions spectrum is discussed. To exhibit the physical structure of the reduced density expansion of N, we Fourier transform to the time domain in Sec. V, and express N using a "time-overlap destruction operator"; the physical meaning of performing approximations on N is then discussed. Our conclusions are summarized in Sec. VI. Various mathematical formulas which we use are derived in four Appendixes.

III. SUMMARY AND DISCUSSION OF PREVIOUS RESULTS

A. Basic Expressions and Definitions

We consider a radiating atom, the system $\mathcal{S}$, immersed in a perturbing gas, the bath $\mathcal{B}$. The whole system $\mathcal{S}+\mathcal{B}$ is assumed in thermal equilibrium initially, with its state specified by the density matrix

$$\rho = e^{-\beta H}/Z\ , \quad Z \equiv \mathrm{Tr}\, e^{-\beta H}\ , \tag{3.1}$$

where H is the total Hamiltonian. The state of $\mathcal{S}$ at time t may be characterized by the operator $\rho e^{itH^\times}$, $e^{itH^\times}$ being the Liouville-space time-evolution operator. We are interested only in the radiator $\mathcal{S}$, the bath being relevant only insofar as it influences $\mathcal{S}$. The state of the "open" system $\mathcal{S}$ can be characterized by "reduced" quantities

$$\sigma \equiv \mathrm{Tr}_B \rho\ , \quad \sigma U(t) = \mathrm{Tr}_B \rho e^{itH^\times}\ , \tag{3.2}$$

where Tr_B (Tr_s) is the trace over bath (system) coordinates, and

$$U(t) \equiv \sigma^{-1}\, \mathrm{Tr}_B \rho e^{itH^\times}\ , \quad U(0) = 1 \tag{3.3}$$

is a non-Hermitian time-evolution operator governing the motion of $\mathcal{S}$ under the influence of the bath.

In order to expand these reduced quantities in powers of the system-bath interaction strength, they are first written in an interaction representation by dividing out their behavior corresponding to absence of the bath: We thus introduce

$$\sigma_I \equiv \rho_s^{-1}\sigma\ , \tag{3.4}$$

$$U_I(t) \equiv U(t) e^{-itH_s^\times}\ , \tag{3.5}$$

where

$$\rho_s = e^{-\beta H_s}/Z_s \;, \quad Z_s \equiv \mathrm{Tr}_s e^{-\beta H_s} \tag{3.6}$$

and $e^{itH_s^\times}$ are, respectively, the reduced-density matrix and time-evolution operator in the absence of the bath. The effect of the bath on the system is specified by the *bath operator*

$$B(t) \equiv \sigma_I U_I(t) = \rho_s^{-1}(\mathrm{Tr}_B \rho e^{itH^\times})\, e^{-itH_s^\times} \;, \tag{3.7}$$

which equals unity in the absence of the bath. $B(t)$ can straightforwardly be expanded in powers of the system-bath interaction or of the gas density, and all relevant quantities will be expressed in terms of it, in order to deduce their expansions from those of $B(t)$. We note in particular,

$$\sigma_I = B(0) \;, \qquad U_I(t) = B(0)^{-1} B(t) \;. \tag{3.8}$$

In terms of $B(t)$, the average value of an S operator A_s at time t is $\mathrm{Tr}_s \rho_s B(t) e^{itH_s^\times} A_s$, and the autocorrelation function of the radiating dipole operator is

$$I(t) = \mathrm{Tr}_s D \rho_s B(t) e^{itH_s^\times} D \;. \tag{3.9}$$

In order to perform its perturbation expansions, we must first express $B(t)$ in a more suitable form. The total Hamiltonian H is written

$$H = H_0 + V \;, \qquad H_0 = H_s + H_B \;,$$

where H_s is the Hamiltonian for the radiator alone, and

$$H_B = \sum_{j=1}^{N} H_j$$

is the sum of one-perturber Hamiltonians, N being the number of perturbing atoms constituting the bath; the interaction

$$V = \sum_{j=1}^{N} V_{sj} + \sum_{i<j} V_{ij} \tag{3.10}$$

is the sum of all interatomic interactions, radiator-perturber (V_{sj}) and perturber-perturber (V_{ij}). We define

$$\rho_B \equiv e^{-\beta H_B}/Z_B \;, \quad Z_B \equiv \mathrm{Tr}_B e^{-\beta H_B} \tag{3.11}$$

the density matrix for the bath with turned-off interactions V_{ij}.

Introducing the complex time $z = t + ib$, and the interaction

$$\begin{aligned} W(z) &= V(z)^\times = V(t)^\times \qquad \text{(on the real } z \text{ axis)} \\ &= V(z) = V(t+ib) \quad \text{(off the real axis)} \;, \end{aligned} \tag{3.12}$$

where

$$V(z) \equiv e^{izH_0} V e^{-izH_0} \;,$$

we write $B(t)$ in the form [Eq. (4.6) of Ref. 1]

$$B(t) = (Z_s Z_B / Z) \langle \exp[i \int_{-i\beta}^{t} dz\, W(z)] \rangle \;; \tag{3.13}$$

$\int_{-i\beta}^{t} dz$ denotes the integral from $-i\beta$ to 0 along the imaginary z axis, and then from 0 to t along the real axis, and

$$\langle (\;) \rangle \equiv \mathrm{Tr}_B \rho_B T_{z^-}(\;) \;, \quad \langle 1 \rangle = 1 \tag{3.14}$$

where T_{z^-} orders operators such that when read from left to right, the arguments z proceed from $-i\beta$ to t along the contour.

By expanding the exponential in (3.13), one obtains the expansion of $B(t)$ in powers of the interaction V, from which may be deduced[1] the corresponding expansions of $R(t)$ and $C(\omega)$. However, we shall be concerned mainly with the expansions in powers of the perturbing gas density, which measures the *average* strength of the system-bath interaction.

B. Reduced-Density Expansions

In Secs. VI and VII of Ref. 1, $B(t)$ and $R(t)$ were expanded in powers of a reduced density, or activity,

$$n = n_B (Z_1 / Z_1^{(T)}) \;, \tag{3.15}$$

where n_B is the perturbing gas density, and $(Z_1^{(T)})^{-1}$ and $(Z_1)^{-1}$ are the perturbing gas fugacities corresponding, respectively, to mutually interacting and noninteracting perturbers. Strict density expansions may be obtained by further introducing the expansion of n in powers of n_B; but only the reduced-density expansions will be considered because they are physically more meaningful. The reduced-density expansions are expressed in terms of quantities of the form

$$\Gamma(-i\beta, z) = \prod_{\mu<\nu}^{(\Gamma)} f_{\mu\nu}(-i\beta, z) \;,$$

where

$$f_{\mu\nu}(-i\beta, z) = \exp[i \int_{-i\beta}^{z} dz'\, W_{\mu\nu}(z')] - 1 \;, \tag{3.16}$$

and the superscript (Γ) on the product symbol specifies the set of pairs (μ, ν) over which the product is taken; the labels $\mu, \; \nu = s, 1, 2, \ldots, N$ can denote the radiator (s) or perturbers ($1, 2, \ldots, N$) (whereas the labels $i, j, \ldots$ only denote perturbers).

A product Γ may be represented by a graph consisting of a white circle labeled s representing the radiator, and black circles labeled $1, 2, \ldots$ representing the perturbers, with each factor $f_{\mu\nu}$ represented by a line or *bond* joining circles μ and ν, indicating that the interaction between these particles is turned on.

We define an *irreducible* graph as a connected graph containing the circle s, which is such that it remains connected after the circle s and the bonds attached to it are removed.

Given any connected graph (or product) Γ containing the radiator, we define

$$i m_\Gamma(-i\beta, z) \equiv \frac{(n\mathcal{V})^{k(\Gamma)}}{\sigma(\Gamma)} \frac{d}{dz} \Gamma(-i\beta, z) \;, \tag{3.17}$$

and in particular,

$$im_{\mu\nu}(-i\beta, z) \equiv n\mathcal{V}\frac{d}{dz}\, f_{\mu\nu}(-i\beta, z)\,, \tag{3.18}$$

where $\mathcal{V}$ is the volume containing the gas, $k(\Gamma)$ is the number of black circles (i.e., perturbers) in the connected graph Γ, and $\sigma(\Gamma)$ is a *symmetry number* characteristic of each graph.[7] We can then write, in the limit $N\to\infty$, $\mathcal{V}\to\infty$, with $N/\mathcal{V}=n_B$ [Eq. (6.12) of Ref. 1, with an over-all multiplicative factor $Z_B^{(T)}Z_s/Z$ neglected]:

$$\begin{aligned}B(\tau) &= \langle i\int_{-i\beta}^{\tau} dz \sum\nolimits^{(\mathrm{conn})} m_\Gamma(-i\beta, z)\rangle \\ &= \langle \exp[i\int_{-i\beta}^{\tau} dz \sum\nolimits^{(\mathrm{irr})} m_\Gamma(-i\beta, z)]\rangle\,, \end{aligned} \tag{3.19}$$

where the sum $\sum^{(\mathrm{conn})}$ is over all topologically distinct *connected* graphs containing the radiator and *some or no* perturbers, while the sum $\sum^{(\mathrm{irr})}$ is over all topologically distinct *irreducible* graphs containing the radiator and *one or more* perturbers. We can also write

$$B(\tau) = \exp_{\rightarrow}[i\int_{-i\beta}^{\tau} dz\, R(-i\beta, z)]\,, \tag{3.20}$$

where

$$\begin{aligned}iR(-i\beta, z) &= \left\langle \frac{d}{dz}\exp\left[i\int_{-i\beta}^{z} dz' \sum\nolimits^{(\mathrm{irr})} m_\Gamma(-i\beta, z')\right]\right\rangle_{c\{m\}} \\ &= \sum\nolimits^{(\mathrm{conn})} \langle im_\Gamma(-i\beta, z)\rangle_{c\{\mathrm{irr}\}}\,; \end{aligned} \tag{3.21}$$

$\langle\ \rangle_{c\{\ \}}$ denotes a *cumulant* average,[8] the argument inside the bracket $\{\ \}$ indicating the elements with respect to which the cumulants are constructed. For instance, if $z_1>z_2>z_3$, and denoting $m_i(-i\beta, z_i)=m_i$, we have

$$\begin{aligned}\langle m_1\rangle_{c\{m\}} &= \langle m_1\rangle\,, \\ \langle m_1m_2\rangle_{c\{m\}} &= \langle m_1m_2\rangle - \langle m_2\rangle\langle m_1\rangle\,, \\ \langle m_1m_2m_3\rangle_{c\{m\}} &= \langle m_1m_2m_3\rangle - \langle m_2m_3\rangle\langle m_1\rangle \\ &\quad - \langle m_3\rangle\langle m_1m_2\rangle - \langle m_2\rangle\langle m_3m_1\rangle \\ &\quad + \langle m_3\rangle\langle m_2\rangle\langle m_1\rangle + \langle m_2\rangle\langle m_3\rangle\langle m_1\rangle\,; \end{aligned}$$

the cumulants $\langle\ \rangle_{c\{\mathrm{irr}\}}$ are similarly constructed with the irreducible components of the connected products Γ as elements.

The reduced-density expansion[9] $R=\sum n^k R^{(k)}$ is readily deduced from (3.21); the kth-order term is

$$R^{(k)}(-i\beta, z) = \sum\nolimits^{(\mathrm{conn},k)} \langle m_\Gamma(-i\beta, z)\rangle_{c\{\mathrm{irr}\}}, \tag{3.22}$$

where the sum $\sum^{(\mathrm{conn},k)}$ is over all connected graphs containing the radiator and k perturbers. In particular, we find $(Z_j \equiv \mathrm{Tr}_j e^{-\beta H_j})$

$$\begin{aligned}R^{(1)}(-i\beta, t) &= \langle m_{sj}(-i\beta, t)\rangle \\ &= n(\mathcal{V}/Z_j)e^{\beta H_s}(\mathrm{Tr}_j\, e^{-\beta H_{sj}}\, e^{itH_{sj}^{\times}}\, V_{sj}^{\times})e^{-itH_s^{\times}}\,. \end{aligned} \tag{3.23}$$

By (3.8) and (3.20), the interaction-representation time-evolution operator is

$$U_I(\tau) = \exp_{\rightarrow}[i\int_0^{\tau} dt\, R(-i\beta, t)]\,. \tag{3.24}$$

[Recall that $\int_{-i\beta}^{\tau} = \int_{-i\beta}^{0} + \int_0^{\tau}$, so that $\exp_{\rightarrow}(\int_{-i\beta}^{\tau}) = \exp_{\rightarrow}(\int_{-i\beta}^{0})\exp_{\rightarrow}(\int_0^{\tau})$.] Defining

$$R(t) \equiv e^{-itH_s^{\times}}R(-i\beta, t)e^{itH_s^{\times}}\,, \tag{3.25}$$

we recover expression (2.3) for the time-evolution operator $U(\tau)=U_I(\tau)e^{itH_s^{\times}}$, namely,

$$U(\tau) = \exp_{\rightarrow}\{i\int_0^{\tau} dt\,[H_s^{\times}+R(t)]\}\,. \tag{3.26}$$

C. Discussion

In the quantities $m_\Gamma(-i\beta, z)$, $R^{(k)}(-i\beta, z)$, etc., the argument $-i\beta$ indicates the "time" at which the interactions are turned on; the interactions taking place from $-i\beta$ to 0 build up the initial correlations between the particles involved, and the real-time interactions affect the motion of the particles. More general quantities in which the interactions are turned on at any time $(-i\beta+t)$ may be introduced by performing appropriate time translations: We first define

$$\begin{aligned}f_{\mu\nu}(-i\beta+t, z) &\equiv e^{itH_0^{\times}}f_{\mu\nu}(-i\beta, z-t)e^{-itH_0^{\times}} \\ &= \exp[i\int_{-i\beta+t}^{z} dz'\, W_{\mu\nu}(z')] - 1\,, \end{aligned} \tag{3.27}$$

where the integral $\int_{-i\beta+t}^{\tau} dz$ is from $-i\beta+t$ to t parallel to the imaginary z axis, and then from t to τ along the real axis. The quantities $m_\Gamma(-i\beta+t, z)$, $R^{(k)}(-i\beta+t, z)$, etc., are then obtained from the corresponding quantities with $t=0$, by replacing all factors $f_{\mu\nu}(-i\beta, z)$ by $f_{\mu\nu}(-i\beta+t, z)$, that is, by replacing all initial times $-i\beta$ by $-i\beta+t$ in expressions (3.16)–(3.23). Formula (3.27) implies

$$m_\Gamma(-i\beta+t, z) = e^{itH_0^{\times}}m_\Gamma(-i\beta, z-t)e^{-itH_0^{\times}}$$

and, because of the relation

$$\langle e^{itH_0^{\times}}(\ )e^{-itH_0^{\times}}\rangle = e^{itH_s^{\times}}\langle(\ )\rangle e^{-itH_s^{\times}}\,,$$

we have

$$\begin{aligned}\langle m_\Gamma(-i\beta+t, z)\rangle_{c\{\mathrm{irr}\}} &= e^{itH_s^{\times}}\langle m_\Gamma(-i\beta, z-t)\rangle_{c\{\mathrm{irr}\}}e^{-itH_s^{\times}}\,, \\ R^{(k)}(-i\beta+t, z) &= e^{itH_s^{\times}}R^{(k)}(-i\beta, z-t)e^{-itH_s^{\times}}\,, \end{aligned} \tag{3.28}$$

etc. According to (3.25) then,

$$R(t) = R(-i\beta-t, 0)\,. \tag{3.29}$$

Let us now consider the simplest type of operator $m_\Gamma(-i\beta+t, \tau)$, namely,[10]

$$\begin{aligned}(n\mathcal{V})^{-1}m_{\mu\nu}(-i\beta+t, \tau) &= i^{-1}\frac{d}{d\tau}\, f_{\mu\nu}(-i\beta+t, \tau) \\ &= \exp[i\int_{-i\beta+t}^{\tau} dz\, W_{\mu\nu}(z)]\, W_{\mu\nu}(\tau)\,. \end{aligned}$$

Because it is proportional to its latest interaction, $m_{\mu\nu}(-i\beta+t, \tau)$ must operate on states such that particles μ and ν are effectively interacting at time τ, in order not to vanish. Since, on the other hand, the interaction or collision of the two particles has a finite duration of maximum length $t_{\mu\nu}$ say, it follows that if $\tau - t > t_{\mu\nu}$, the collision, which must still be in process at τ, started *later* than the time t at which the interaction was turned on; this means that $m_{\mu\nu}(-i\beta + t, \tau)$ becomes *independent* of t once t is earlier than $\tau - t_{\mu\nu}$, and we can write

$$\tau - t > t_{\mu\nu} \Rightarrow m_{\mu\nu}(-i\beta + t, \tau) = m_{\mu\nu}(-\infty, \tau) \ . \qquad (3.30)$$

The time-independent operator $m_{\mu\nu}(-\infty, 0)$ has the structure of a T matrix, and may be called a Liouville-space T matrix for scattering of particles μ and ν.

It was argued in Appendix D of Ref. 1 that if Γ is an irreducible graph, then for $\langle m_\Gamma(-i\beta + t, \tau)\rangle$ not to vanish, the interactions it contains must be clustered around time τ; in fact, this can be shown rigorously only if less than three perturbers are involved (see Ref. 22). Thus for $\tau - t$ greater than some t_Γ and $k(\Gamma) \leq 2$, we have

$$\tau - t > t_\Gamma \Rightarrow \langle m_\Gamma(-i\beta + t, \tau)\rangle = \langle m_\Gamma(-\infty, \tau)\rangle \qquad (\Gamma \text{ irreducible}) \ , \qquad (3.31)$$

t_Γ being the maximum duration of multiple collisions of type Γ.

If Γ is connected, but not irreducible, then in $\langle m_\Gamma(-i\beta + t, \tau)\rangle_{c\{\text{irr}\}}$, the cumulant average forces the irreducible components of Γ to be connected *in time*, thus forming one large multiple collision of maximum duration t_Γ, and we have the generalization of (3.31): for $k(\Gamma) \leq 2$,

$$\tau - t > t_\Gamma \Rightarrow \langle m_\Gamma(-i\beta + t, \tau)\rangle_{c\{\text{irr}\}} = \langle m_\Gamma(-\infty, \tau)\rangle_{c\{\text{irr}\}} \qquad (\Gamma \text{ connected}) \ , \qquad (3.32)$$

which implies in turn, for $k \leq 2$,

$$\tau - t > t_{(k)} \Rightarrow R^{(k)}(-i\beta + t, \tau) = R^{(k)}(-\infty, \tau) \ , \qquad (3.33)$$

where $t_{(k)}$ is the maximum duration of multiple collisions of the radiator with k perturbers.

Each operator $\langle m_\Gamma(-i\beta + t, \tau)\rangle_{c\{\text{irr}\}}$ corresponds to a particular type of multiple collision; the operator $R = \sum^{(\text{conn})} \langle m_\Gamma\rangle_{c\{\text{irr}\}}$ thus appears as a sum over all types of multiple collisions, that is, over all *mutually independent*, or *uncorrelated*, processes by which the radiator can interact with the bath. To further elucidate the physical significance of R, or rather of the terms $R^{(k)}$ of its expansion, let us consider the reduced-density expansion of $U_I(\tau)$ as deduced from (3.24):

$$U_I(\tau) = 1 + \int_0^\tau dt\, iR^{(1)}(-i\beta, t) + \int_0^\tau dt\, \Big[iR^{(2)}(-i\beta, t) + \int_0^t dt'\, iR^{(1)}(-i\beta, t')\, iR^{(1)}(-i\beta, t) \Big] + \cdots \ . \qquad (3.34)$$

This expansion may be interpreted as a sum over possible histories in the interval $(0, \tau)$: The zeroth-order term 1 corresponds to no interaction of the radiator with the bath in $(0, \tau)$. The first-order term corresponds to the radiator interacting with one perturber in $(0, \tau)$. The second-order term corresponds to the radiator interacting with two perturbers in $(0, \tau)$; it consists of two parts: The term $\int\int R^{(1)} R^{(1)}$ represents two independent collisions of the radiator with single perturbers; this independent-collisions term would be sufficient if the two collisions never overlapped in time, in which case their combined contribution is simply the product of the contributions of each. But if the collisions overlap in time, the two perturbers interact with each other, and also their individual interactions $W_{\mu\nu}$ with the radiator get time-entangled because of the time ordering; it is the term $\int R^{(2)}$ which accounts for these effects. The terms of higher order in the expansion of U_I are constructed and interpreted in a similar manner. Clearly then, when one retains only the first-order term $R^{(1)}$ in the expansion of R, one neglects all correlations between the perturbers; by adding the second-order term $R^{(2)}$, one allows for correlated pairs of perturbers, and similarly for higher-order approximations.

The independent-collision approximation $R \rightarrow R^{(1)}$ is strictly correct in the low-density limit where (almost) only binary collisions occur. But it may still constitute a reasonably accurate approximation at higher densities where multiple collisions occur with an appreciable frequency: In particular, the independent-collision spectrum does contain the effect of simultaneous interactions of the radiator with several perturbers, though treated in an approximate manner. As already noted in the context of the adiabatic theory of pressure broadening,[6] the main effect of multiple collisions is the (experimentally observed) pressure-dependent shift of the wing structure of the spectrum, plus possible additional fine structure. To see this in the more general context considered here, let us make use of formula (B1) of Appendix B, and write the Fourier transform of $U(\tau)$ as given by (3.26) in the form $(\omega \equiv \omega - H_s^\times)$.

$$iU(\omega) = \frac{1}{\hat{\omega}} + \left[\frac{1}{\hat{\omega}} * R(\omega)\right] \frac{1}{\hat{\omega}} + \left[\left[\left[\frac{1}{\hat{\omega}} * R(\omega)\right] \frac{1}{\hat{\omega}}\right] * R(\omega)\right] \frac{1}{\hat{\omega}} + \cdots \ . \qquad (3.35)$$

The propagators $(1/\hat{\omega})$ represent free motion of the system $\mathcal{S}$; all the frequency dependence introduced by its interaction with the bath is contained in the "interactions" $R(\omega)$. At large values of t, $R(t)$ is assumed to tend to a constant

$$\bar{R} = \lim_{T \to \infty} (1/T) \int_0^T dt\, R(t) \ , \qquad (3.36)$$

upon which may be superposed oscillatory terms due to formation of radiator-perturber bound states (in the following, we may also think of R as treated to first or second order of n, since $R^{(1)}$ and $R^{(2)}$ *have* the asymptotic behavior assumed above for R). The Fourier transform $\overline{R}/i\omega$ of $\overline{R}$ diverges at the origin, and causes the successive terms in the expansion (3.35) to diverge at $\hat{\omega}=0$ as increasing powers[11] of $(1/\hat{\omega})$. To obtain a well-behaved expansion,[12] we write $R(\omega)=\overline{R}/i\omega+\tilde{R}(\omega)$, where

$$\tilde{R}(t)\equiv R(t)-\overline{R}\ , \tag{3.37}$$

and *resum* (3.35) into the form

$$iU(\omega)=\frac{1}{\omega-\mathfrak{L}}+\left[\frac{1}{\omega-\mathfrak{L}}*\tilde{R}(\omega)\right]\frac{1}{\omega-\mathfrak{L}}+\left[\left[\left[\frac{1}{\omega-\mathfrak{L}}*\tilde{R}(\omega)\right]\frac{1}{\omega-\mathfrak{L}}\right]*\tilde{R}(\omega)\right]\frac{1}{\omega-\mathfrak{L}}+\cdots\ , \tag{3.38}$$

where

$$\mathfrak{L}\equiv H_s^{\times}+\overline{R}\ . \tag{3.39}$$

Expression (3.38) can also be obtained by writing $H_s^{\times}+R(t)=\mathfrak{L}+\tilde{R}(t)$ in (3.26), and then using formula (B1) to take the Fourier transform.

The operators $\tilde{R}(\omega)$ are regular at the origin, and they contain all the fine structure due to interaction with the bath, such as satellites[13] and bound spectra. In the propagators $(\omega-\mathfrak{L})^{-1}=(\omega-H_s^{\times}-\overline{R})^{-1}$, the oscillation frequencies $H_s^{\times}$ of $\mathcal{S}$ are shifted and broadened by the amount $\overline{R}$; these propagators combine with the interactions $\tilde{R}(\omega)$ by means of *convolutions*, and since the *shift-width operator* $\overline{R}$ increases with the gas pressure, it follows that the whole spectrum, including the wings due to $\tilde{R}(\omega)$, gets shifted and broadened under increasing pressure. This remains true if one approximates R by $R^{(1)}$ everywhere in (3.38). One may view $\tilde{R}^{(1)}(\omega)$ as the spectrum of the radiator while interacting with a perturber, thus forming a molecule; this molecular spectrum is broadened and shifted by the interaction with the rest of the bath. Also, larger molecules are formed during multiple collisions, and their spectrum is given, in the independent-collision approximation, by convolutions of the spectra of each component binary radiator-perturber molecule. In such convolution products, the fine structure of each factor $\tilde{R}^{(1)}(\omega)$ may combine to give additional fine structure[14]; for instance, if $\tilde{R}^{(1)}(\omega)$ has a pole at a bound-spectrum frequency ω_b then, as indicated in Ref. 11, the successive terms in (3.38) have broadened and shifted poles at the frequencies $2\omega_b$, $3\omega_b$, ...

IV. FREQUENCY-DOMAIN RELATIONS

Defining the operator frequency

$$\hat{\omega}\equiv\omega-H_s^{\times}\ , \tag{4.1}$$

namely, the frequency measured relative to the unperturbed frequencies of $\mathcal{S}$, we have

$$U(\omega)=U_I(\hat{\omega})\ , \tag{4.2}$$

where we define, for any operator $F(\tau)$,

$$F(\hat{\omega})\equiv\int_0^{\infty}d\tau\,F(\tau)e^{-i\hat{\omega}\tau}\ . \tag{4.3}$$

Equations (2.4) and (2.6) are then written

$$iU_I(\hat{\omega})=[\hat{\omega}-C(\omega)]^{-1}\ , \tag{4.4}$$

$$C(\omega)=\hat{\omega}-[iU_I(\hat{\omega})]^{-1}=\hat{\omega}(1-\{1+[U_I(\hat{\omega})i\hat{\omega}-1]\}^{-1}) \tag{4.5}$$

where, for the purpose of constructing its density expansion from that of U, $C(\omega)$ is expressed in terms of the quantity

$$M(\hat{\omega})\equiv U_I(\hat{\omega})i\hat{\omega}-1\ ,$$

which vanishes in the absence of the bath. From the relation $[\dot{F}(\tau)\equiv dF/d\tau]$

$$\dot{F}(\hat{\omega})\equiv\int_0^{\infty}d\tau\,\dot{F}(\tau)e^{-i\hat{\omega}\tau}=-F(\tau=0)+F(\hat{\omega})i\hat{\omega}\ , \tag{4.6}$$

it follows that[15] [note that $U_I(\tau=0)=1$]

$$M(\tau)=\dot{U}_I(\tau)\ ; \tag{4.7}$$

$M(\tau)$ is of the same general type as the operators m of Sec. III, namely, the time derivative of an interaction-representation time-evolution operator. Introducing $N(\hat{\omega})$ by the relation[16]

$$C(\omega)=\hat{\omega}N(\hat{\omega})\ , \tag{4.8}$$

we write Eq. (4.5) in the form

$$N(\hat{\omega})=1-[1+M(\hat{\omega})]^{-1}=M(\hat{\omega})/[1+M(\hat{\omega})]=[M(\hat{\omega})^{-1}+1]^{-1} \tag{4.9}$$

or, equivalently,

$$[1+M(\hat{\omega})]=[1-N(\hat{\omega})]^{-1}\ . \tag{4.10}$$

Equations (4.9) and (4.10) are perfectly symmetric in M and $-N$; thus, any expression of M in terms of N is inverted by simply interchanging M with $-N$, and vice versa.

The reduced-density expansion of N is obtained from that of $M=nM^{(1)}+n^2M^{(2)}+\cdots$, namely,

$$N(\hat{\omega})=nM^{(1)}+n^2[M^{(2)}-M^{(1)}M^{(1)}]+\cdots\ ; \tag{4.11}$$

the first-order term is given by [cf. Eqs. (4.7) and (3.24)]

$$N^{(1)}(\tau)=M^{(1)}(\tau)=iR^{(1)}(-i\beta,\tau)=ie^{i\tau H_s^{\times}}R^{(1)}(\tau)\,e^{-i\tau H_s^{\times}}\ , \tag{4.12}$$

whence

$$N^{(1)}(\hat{\omega})=iR^{(1)}(\hat{\omega}_{\leftarrow})\equiv i\int_0^{\infty}d\tau\,e^{-i\hat{\omega}\tau}R^{(1)}(\tau)\ , \tag{4.13}$$

where, for any operator $F(\tau)$, we define

$$F(\hat{\omega}_{\leftarrow})\equiv\int_0^{\infty}d\tau\,e^{-i\hat{\omega}\tau}F(\tau)=(1/i\hat{\omega})*F(\omega)\ . \tag{4.14}$$

(The arrow indicates on which side of F the operator $\hat{\omega}$ appears.[17])

In the approximation $N \to N^{(1)}$, we have

$$U(\omega)=\{i\hat{\omega}[1-iR^{(1)}(\hat{\omega}_{-})]\}^{-1} . \tag{4.15}$$

We expand

$$iU(\omega)=(1/\hat{\omega})+iR^{(1)}(\hat{\omega}_{-})(1/\hat{\omega})+[iR^{(1)}(\hat{\omega}_{-})]^2(1/\hat{\omega})+\cdots \tag{4.16}$$

and compare with Eq. (3.35) in which the approximation $R \to R^{(1)}$ is made [call the result Eq. (3.35a)]. The two first terms of (4.16) are identical to those of (3.35a), but the succeeding terms involve only powers of $R^{(1)}(\hat{\omega}_{-})$, and consequently all have essentially the same *shape* as $R^{(1)}(\hat{\omega}_{-})$, unlike the terms of (3.35a), which involve multiple convolutions of $R^{(1)}(\omega)$ with itself, and which may therefore be of very different shape from $R^{(1)}(\omega)$, leading to the pressure shift and additional structure of the wings. It thus appears that (4.15), whose shape (in the wings) is essentially that of the one perturber $R^{(1)}(\hat{\omega}_{-})$, does not contain multiple-collision effects, as will be discussed in more detail in Sec. V. In Appendix E, it is further shown that in the far wings, the line shape $\mathrm{Re}I(\omega)$ derived from (4.15) equals the one-perturber line shape.

We note that we may write $B(\hat{\omega})=\sigma_I U(\omega)$ in resolvent form as follows, so as to put all the effect of the bath in the denominator:

$$\begin{aligned} B(\hat{\omega}) &= B(0)[i\hat{\omega}-iC(\omega)]^{-1} \\ &= [i\hat{\omega}B(0)^{-1}-iC(\omega)B(0)^{-1}]^{-1} . \end{aligned} \tag{4.17}$$

[Recall that $\sigma_I=B(0)$.] One may treat the denominator to first order in the gas density, by using the expansions $C=C^{(1)}+C^{(2)}+\cdots$ and $B(0)=1+B^{(1)}(0)+B^{(2)}(0)+\cdots$, the latter being deduced from the first line of (3.19); we have then

$$B(\hat{\omega})=\{i\hat{\omega}[1-B^{(1)}(0)]-iC^{(1)}(\omega)\}^{-1} .$$

V. TIME-DOMAIN RELATIONS

In order to exhibit the physical structure of the reduced-density expansion of N, the relations of Sec. IV are written in the time domain by Fourier transforming. As shown in Appendix D, Eq. (4.9) is equivalent to the integral equation

$$M(t,\tau)=N(t,\tau)+\int_t^\tau ds\, M(t,s)N(s,\tau) , \tag{5.1}$$

where double-time operators $F(t,\tau)$ are defined in terms of single-time operators $F(\tau)$ by means of the correspondence

$$F(t,\tau)\equiv e^{itH_S^\times}F(\tau-t)e^{-itH_S^\times} . \tag{5.2}$$

Thus, by (4.7), (3.24), and (3.28) we find [to simplify notation, we sometimes write $R(-i\beta+t,s)\equiv R(t,s)$] :

$$M(t,\tau)=\exp_{\leftarrow}\Big[i\int_t^\tau ds\, R(t,s)\Big]R(t,\tau) . \tag{5.3}$$

Equation (5.1) can be solved iteratively for M in terms of N, or for N in terms of M; as already noticed on its Fourier transform (4.9), (5.1) is perfectly symmetric in M and $-N$, and expressions of M in terms of N are inverted by simply interchanging M with $-N$. Solutions of (5.1) are written in several different manners in Appendix D.

According to (5.3), $M(t,\tau)$ is of the form (D10) (with $P=1$), and we can make use of formula (D11) to write

$$N(t,\tau)=\exp_{\leftarrow}\Big[i\int_t^\tau ds\, R(t,s)(1-\Lambda)\Big]R(t,\tau) , \tag{5.4}$$

where the "time-overlap destruction operator" Λ is defined as follows: Appearing inside a product of operators $R(-i\beta+t_i,\tau_i)$, Λ makes *all* those t_i's on its *right*-hand side which are *smaller than*, *equal* to the *largest* τ_i on its *left*-hand side; for instance, if $t<s<\tau$,

$$R(-i\beta+t,s)\Lambda R(-i\beta+t,\tau)=R(-i\beta+t,s)R(-i\beta+s,\tau) .$$

The reduced-density expansion of $N(t,\tau)$ is obtained by inserting the expansion of R into (5.4):

$$\begin{aligned} N(t,\tau) &= nR^{(1)}(t,\tau)+n^2[R^{(2)}(t,\tau) \\ &\quad +i\int_t^\tau ds\, R^{(1)}(t,s)(1-\Lambda)R^{(1)}(t,\tau)]+\cdots . \end{aligned} \tag{5.5}$$

We write explicitly, for instance, the second term in the coefficient of n^2, namely,

$$i\int_t^\tau ds\,[R^{(1)}(t,s)R^{(1)}(t,\tau)-R^{(1)}(t,s)R^{(1)}(s,\tau)] .$$

The general term in (5.5) is of the form (we set $\tau\equiv s_m$)

$$\begin{aligned} &\int_t^{s_m} ds_{m-1}\int_t^{s_{m-1}} ds_{m-2}\cdots\int_t^{s_2} ds_1\, A_1(t,s_1) \\ &\quad \times(1-\Lambda)A_2(t,s_2)(1-\Lambda)\ldots(1-\Lambda)A_m(t,s_m); \end{aligned} \tag{5.6}$$

if it is assumed that each $A_i(t,s_i)$ becomes independent of t once $(s_i-t)>t_{(i)}$, then (5.6) becomes independent of t as $\tau-t\to\infty$; indeed, let $t_{\max}$ be the largest of these $t_{(i)}$'s: The integrand in (5.6) vanishes whenever for some i, $s_{i+1}-s_i>t_{\max}$, for then $A_j(s_i,s_j)=A_j(t,s_j)$ for all $j>i$, so that the operator Λ appearing between A_i and A_{i+1} does not change anything; i.e., it has the same effect as the operator 1 from which it is subtracted. Thus, all the s_i's must be *clustered* within a time interval smaller than $mt_{\max}$ for the integrand not to vanish, which implies that (5.6) becomes independent of t as $\tau-t\to\infty$.

[*Note added in proof*. Thus, the (assumed) existence of $R(t,\tau)$ in the limit $t\to-\infty$ implies that each term in the expansion (5.4) of $N(t,\tau)$ in powers of R also exists in that limit {the existence of $N(t,\tau)$ as $t\to-\infty$ is required for $C(\omega)=\hat{\omega}N(\hat{\omega})$ not to diverge at values of ω equal to eigenfrequencies of

$H_s^\times$ [note that $N(\hat{\omega}) \equiv \int_0^\infty dt\, N(t) e^{-i\hat{\omega}t} = \int_0^\infty dt\, e^{-i\hat{\omega}t} \times N(-t, 0)]\}$. As for the density expansion (5. 5) of $N(t, \tau)$, it is free, as is that of $R(t, \tau)$, of the "worst" secularities present in the expansion of $U(\tau)$, namely, those arising from successions of uncorrelated collisions. Because $R^{(1)}(t, \tau)$ and $R^{(2)}(t, \tau)$ exist in the limit $t \to -\infty$, the same holds for the terms of order n and n^2 in (5. 5), and $N(t, \tau)$ may therefore be approximated by these two terms only (it is not clear how one can obtain higher-order approximations[22]). If one treats R to first or second order in (5. 5), one obtains a density expansion in which each term exists in the limit $t \to -\infty$; in particular, by making $R \to R^{(1)}$ in (5. 4), or (5. 5), we obtain $N(t, \tau)$ in the "independent-collision approximation," expressed as a uniformly convergent expansion in powers of $nR^{(1)}$.]

We now wish to investigate what is the physical meaning of approximating N by its first-order term $R^{(1)}$; for this purpose, we recall Eqs. (5.1) and (4.7), and make use of formula (D9) of Appendix D to write

$$U_I(\tau) = \exp_{\leftarrow}\left[i \int_0^\tau ds\, \Lambda N(0, s)\right] . \qquad (5.7)$$

Inserting the approximation $N \to R^{(1)}$ in (5.7), and comparing with the exact expression (3.34) of $U_I(\tau)$, we first note that in neglecting all $R^{(k)}$'s of order > 1, we neglect all correlations between perturbers, i.e., we make the independent-collision approximation; we note furthermore that the operators Λ ensure that in each term of the form

$$\int_0^\tau ds_{m-1} \int_0^{s_{m-1}} ds_{m-2} \ldots \int_0^{s_2} ds_1\, \Lambda R^{(1)}(-i\beta, s_1)\Lambda \ldots \Lambda R^{(1)}(-i\beta, s_{m-1})$$
$$= \int_0^\tau ds_{m-1} \int_0^{s_{m-1}} ds_{m-2} \ldots \int_0^{s_2} ds_1\, R^{(1)}(-i\beta, s_1) R^{(1)}(-i\beta + s_1, s_2) \ldots R^{(1)}(-i\beta + s_{m-2}, s_{m-1}), \qquad (5.8)$$

the different binary-collision factors $R^{(1)}(-i\beta + s_{i-1}, s_i)$ span mutually *nonoverlapping* time intervals (s_{i-1}, s_i), that is, the interactions of the radiator with each perturber are turned on one at a time.[18] This implies that effects due to the simultaneous interaction of the radiator with several perturbers will not appear in the spectrum calculated with the approximation $N \to N^{(1)}$, as already observed in Sec. IV, and shown more explicitly in Appendix E.

The significance of the terms of higher order in the reduced-density expansion of N is now clear: For instance, the third term in (5. 5) is the contribution from the overlapping part of the simultaneous interaction of the radiator with two mutually independent perturbers, and the term $R^{(2)}$ is the correction due to the mutual correlation of the two perturbers. Thus, by adding the term $N^{(2)}$ to the approximation $N \to N^{(1)}$, one allows the radiator to feel two perturbers simultaneously, with these two perturbers also feeling each other, and similarly with higher-order approximations.

We note finally that the expression of $N(\tau)$ is somewhat simpler if one neglects *initial correlations* between atoms, i.e., takes $\rho = e^{-\beta H_0}/\mathrm{Tr}\, e^{-\beta H_0} = \rho_s \rho_B$. In this case, $B(0) = 1$, and by (3. 8), (3. 19), and (4. 7),

$$M(\tau) = \dot{U}_I(\tau) = \dot{B}(\tau) = \frac{d}{d\tau} \exp_{\leftarrow}\left[i \int_0^\tau ds \sum{}^{(\mathrm{irr})} m_\Gamma(0, s)\right] P , \qquad (5.9)$$

where

$(\ldots)P \equiv \langle(\ldots)\rangle$ (P operates on the left-hand side) .

Then, by (D11), we can write

$$N(\tau) = \exp_{\leftarrow}\left[i \int_0^\tau ds \sum{}^{(\mathrm{irr})} m_\Gamma(0, s)(1 - P\Lambda)\right] \times \sum{}^{(\mathrm{irr})} m_\Gamma(0, \tau) P . \qquad (5.10)$$

VI. CONCLUSION

The motion of a system $\mathcal{S}$ in contact with a bath can be described by means of a nonunitary time-evolution operator $U(t)$ acting in the Liouville space of $\mathcal{S}$. The perturbation expansions of $U(t)$ do not converge uniformly and cannot be truncated; in order to perform approximations, we express $U(t)$ as a functional $F[L(t)]$ of some quantity L which has expansions that can be truncated. There are several possible such functions L, and one must choose those for which the relation F is sufficiently simple and practical. At the end of Appendix D, an example is found of an $L(t)$ which has suitable expansions, but for which the relation F is of no practical value. Two forms of F have been considered, namely, an *ordered exponential* $U(t) = \exp_{\leftarrow}[i \int_0^t dt'\, L_1(t')]$ and a *resolvent* form $iU(\omega) = [\omega - L_2(\omega)]^{-1}$. We investigated the physical structure of the reduced-density expansions of L_1 and L_2, and the physical significance of approximating these expansions by their first few terms. It was seen in Ref. 1 that by treating L_1 to first order in the reduced density, one effectively assumes mutually independent perturbers, whereas by treating L_2 to the same order, we saw in this paper that one allows the radiator to interact with only one perturber at a time. These differences reflect themselves in the corresponding expressions of the spectrum: Multiple-collision effects are absent in the second case, but present in the first case, though treated approximately, resulting principally in the pressure shift of the wing structure. Thus, the independent-collision approximation is better than the nonoverlapping–interactions approximation, but on the other hand, the resolvent form is more practical for calculations than the ordered-exponential form.

In the ordered-exponential and resolvent approaches, we replace the unperturbed Liouvillian $H_s^\times$ of the system by time- and frequency-dependent effective Liouvillians $L_1(t)$ and $L_2(\omega)$, respectively; time being a more "physical" variable than the frequency ω, it is expected that $L_1(t)$ will have a more physical significance than $L_2(\omega)$. Indeed, the expression of $U(t)$ in terms of the reduced-density expansion of $L_1(t)$ seems the most "natural," for it breaks up the interaction of the system $\mathcal{S}$ with the bath into its elementary mutually independent processes; and it also proved advantageous[19] to also express $L_2(\omega)$ in terms of the $R^{(k)}$'s.

ACKNOWLEDGMENTS

The author wishes to thank Professor K. M. Van Vliet, Dr. A. Friedman, and Dr. Bui-Duy Quang for helpful discussions.

APPENDIX A: CONVOLUTION PRODUCTS AND FOURIER TRANSFORMS

Given operators $A(t_1, t_2)$, $B(t_1, t_2)$, ... depending on two time arguments, we define a double-time convolution product denoted by $*$:

$$A * B(t, \tau) \equiv \int_{-\infty}^{\infty} ds\, A(t, s)\, B(s, \tau) \;. \qquad \text{(A1)}$$

This is essentially a matrix product, and is clearly associative,

$$(A * B) * C = A * (B * C) = A * B * C \;,$$

since, for instance,

$$\begin{aligned}(A * B) * C(t, \tau) &= \int ds\, (A * B)(t, s) C(s, \tau) \\ &= \int ds \int ds'\, A(t, s') B(s', s) C(s, \tau) \;.\end{aligned}$$

In general,

$$\begin{aligned}A_1 * A_2 * \cdots * A_k(t, \tau) = \int ds_1 \int ds_2 \ldots \int ds_{k-1} A_1(t, s_1) \\ \times A_2(s_1, s_2) \ldots A_k(s_{k-1}, \tau) \;. \qquad \text{(A2)}\end{aligned}$$

The unit for this product is the Dirac δ function $\delta(t, \tau) = \delta(\tau - t)$:

$$A * \delta(t, \tau) = \int ds\, A(t, s) \delta(s, \tau) = A(t, \tau) \;.$$

We note that if $A_i(t, \tau)$ vanishes when $\tau - t < 0$, we can write

$$A_1 * A_2(t, \tau) = \int_t^\tau ds\, A_1(t, s) A_2(s, \tau) \;, \qquad \text{(A3)}$$

$$\begin{aligned}A_1 * A_2 * \cdots * A_k(t, \tau) &= \int_t^\tau ds_{k-1} \int_t^{s_{k-1}} ds_{k-2} \ldots \int_t^{s_2} ds_1 \\ &\quad \times A_1(t, s_1) A_2(s_1, s_2) \ldots A_k(s_{k-1}, \tau) \\ &= \int_t^\tau ds_1 \int_{s_1}^\tau ds_2 \ldots \int_{s_{k-2}}^\tau ds_{k-1} \\ &\quad \times A_1(t, s_1) A_2(s_1, s_2) \ldots A_k(s_{k-1}, \tau) \;. \qquad \text{(A4)}\end{aligned}$$

In case $A_i(t, \tau) = A_i(\tau - t)$ are functions of $\tau - t$, the convolution product defined above reduces to the usual (single-time) convolution product

$$A_1 * A_2(t, \tau) = A_1 * A_2(\tau - t) = \int ds\, A_1(s) A_2(\tau - t - s) \;.$$

As is well known, the Fourier transform of an ordinary (single-time) convolution product equals the (ordinary) product of the Fourier transforms of each factor:

$$\mathfrak{F}\{A * B(\tau)\} \equiv \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} A * B(\tau) = A(\omega) B(\omega) \;. \qquad \text{(A5)}$$

If we now define

$$A(\hat{\omega}) \equiv \int_{-\infty}^{\infty} d\tau\, A(\tau)\, e^{-i\hat{\omega}\tau} \equiv \hat{\mathfrak{F}}\{A(\tau)\} \;, \qquad \text{(A6)}$$

where $\hat{\omega}$ is an *operator* frequency not commuting with the operators A and B, we can have a result analogous to (A5) by defining double-time operators $A(t, \tau)$ in terms of the single-time $A(\tau)$ by means of the prescription

$$A(t, \tau) \equiv e^{-i\hat{\omega}t} A(\tau - t) e^{i\hat{\omega}t} \;; \qquad \text{(A7)}$$

then,

$$\begin{aligned}\hat{\mathfrak{F}}\{A * B(0, \tau)\} &= \int d\tau\, A * B(0, \tau) e^{-i\hat{\omega}\tau} \\ &= \int d\tau \int ds\, A(0, s) B(s, \tau) e^{-i\hat{\omega}\tau} \\ &= \int ds\, A(0, s) e^{-i\hat{\omega}s} \int d\tau\, B(0, \tau - s) \\ &\qquad \times e^{-i\hat{\omega}(\tau - s)} \;,\end{aligned}$$

that is

$$\hat{\mathfrak{F}}\{A * B(0, \tau)\} = A(\hat{\omega}) B(\hat{\omega}) \;. \qquad \text{(A8)}$$

By the associativity of the double-time convolution product, we have, more generally,

$$\hat{\mathfrak{F}}\{A_1 * A_2 * \cdots * A_k(0, \tau)\} = A_1(\hat{\omega}) A_2(\hat{\omega}) \ldots A_k(\hat{\omega}) \;.$$

APPENDIX B: FOURIER TRANSFORM OF $\exp_{\rightarrow}\{i \int_0^\tau dt[\Omega + F(t)]\}$

We have

$$\begin{aligned}\exp_{\rightarrow}\{i \int_0^\tau dt[\Omega + F(t)]\} &= \exp_{\rightarrow}[i \int_0^\tau dt\, e^{it\Omega} F(t) e^{-it\Omega}]\, e^{i\tau\Omega} \\ &= e^{i\tau\Omega} + i \int_0^\tau dt\, e^{it\Omega} F(t) e^{i(\tau - t)\Omega} + \\ &\qquad \cdots + i^k G^{(k)}(\tau) + \cdots \;,\end{aligned}$$

where

$$\begin{aligned}G^{(k)}(\tau) &= \int_0^\tau dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{k-1}} dt_k\, e^{it_k\Omega} F(t_k) e^{-it_k\Omega} \ldots \\ &\qquad \times e^{it_1\Omega} F(t_1) e^{i(\tau - t_1)\Omega} \\ &= \int_0^\tau dt_1\, G^{(k-1)}(t_1) F(t_1) e^{i(\tau - t_1)\Omega} \\ &= [G^{(k-1)}(\tau) F(\tau)] * [e^{i\tau\Omega}] \;,\end{aligned}$$

$$G^{(0)}(\tau)=e^{i\tau\Omega} .$$

(As usual, all functions of τ are understood to vanish when $\tau<0$.) Fourier transformed, the above equations read

$$G^{(k)}(\omega)=[G^{(k-1)}(\omega)*F(\omega)][1/i(\omega-\Omega)] ,$$

$$G^{(0)}(\omega)=[i(\omega-\Omega)]^{-1} ,$$

whence, setting $\omega-\Omega\equiv\hat{\omega}$,

$$i\int_0^\infty d\tau\, e^{-i\omega\tau}\exp_{-}\{i\int_0^\tau dt[\Omega+F(t)]\}$$

$$=\frac{1}{\hat{\omega}}+\left[\frac{1}{\hat{\omega}}*F(\omega)\right]\frac{1}{\hat{\omega}}+\left[\left[\left[\frac{1}{\hat{\omega}}*F(\omega)\right]\frac{1}{\hat{\omega}}\right]*F(\omega)\right]$$

$$\times\frac{1}{\hat{\omega}}+\cdots . \qquad \text{(B1)}$$

APPENDIX C: PROJECTION-OPERATOR METHOD

In this appendix, Zwanzig's projection-operator method[4] is given in a form suitable for our purposes.

If $M(t,\tau)$ is of the form

$$M(t,\tau)=\frac{d}{d\tau}\exp_{-}\left[\int_t^\tau ds\, V(s)\right]Q$$

$$=\exp_{-}\left[\int_t^\tau ds\, V(s)\right]V(\tau)Q , \qquad \text{(C1)}$$

where Q is a (projection) operator acting on the left-hand side [e.g., $(\;)Q=\langle(\;)\rangle$], satisfying $1Q=1$, then

$$N(t,\tau)=\exp_{-}[\int_t^\tau ds\, V(s)(1-Q)]\, V(\tau)Q \qquad \text{(C2)}$$

satisfies the equation

$$M(t,\tau)=N(t,\tau)+\int_t^\tau ds\, M(t,s)N(s,\tau) . \qquad \text{(C3)}$$

Proof: Call

$$F(t,\tau)\equiv\exp_{-}[\int_t^\tau ds\, V(s)] ,$$

$$F_1(t,\tau)\equiv F(t,\tau)Q ,$$

$$F_2(t,\tau)\equiv F(t,\tau)(1-Q) ;$$

note that

$$F=F_1+F_2 , \quad F_1(t,t)=1 ,$$

$$F_2(t,t)=0 .$$

We have (the dot denotes differentiation with respect to τ)

$$M(t,\tau)=\dot{F}_1(t,\tau)=F(t,\tau)\, V(\tau)Q$$

$$=F_1(t,\tau)V(\tau)Q+F_2(t,\tau)V(\tau)Q ,$$

$$\dot{F}_2(t,\tau)=F_1(t,\tau)V(\tau)(1-Q)+F_2(t,\tau)V(\tau)(1-Q) .$$

The second equation, with the boundary condition $F_2(t,t)=0$, has the solution

$$F_2(t,\tau)=\int_t^\tau ds\, F_1(t,s)V(s)(1-Q)$$

$$\times\exp_{-}\left[\int_s^\tau ds'\, V(s')(1-Q)\right]$$

$$=-\int_t^\tau ds\, F_1(t,s)\frac{d}{ds}\exp_{-}\left[\int_s^\tau ds'\, V(s')(1-Q)\right] ,$$

and the first equation can be written

$$\dot{F}_1(t,\tau)=F_1(t,\tau)V(\tau)Q-\int_t^\tau ds\, F_1(t,s)\frac{d}{ds}N(s,\tau) , \qquad \text{(C4)}$$

where $N(s,\tau)$ is given by (C2). Integrating by parts the second right-hand term of (C4), we recover Eq. (C3).

Equation (C4) is of a familiar form in irreversible statistical mechanics,[4,5] and it is $(d/ds)N(s,\tau)$, which is generally referred to as a "memory operator." The form (C3) has the advantage that it is easily solved for N directly in terms of M (see Appendix D), without requiring the projection-operator method which applies only when M is of a certain type, such as (C1); in our case, for instance, M is not of the type (C1) when initial correlations are included, and one cannot use Zwanzig's method[4] directly. (Fano,[3] who uses an equivalent of Zwanzig's method, neglects initial correlations between atoms.)

We note that Mori's continued-fraction expansion[5(b)] may be obtained by forming a succession of equations of the type (C3): Let us define

$$N_j'(\tau)\equiv\frac{d}{ds}N_j(s,\tau)\Big|_{s=0}$$

and

$$M_j(\tau)\equiv N_j'(0)^{-1}\dot{N}_j'(\tau) ;$$

$\dot{N}_j'(\tau)\equiv(d/d\tau)N_j'(\tau)$, where double-time quantities are related to the corresponding single-time quantities by (A7). We have

$$N_j'(\tau)=\frac{d}{ds}e^{-i\hat{\omega}s}N_j(\tau-s)e^{i\hat{\omega}s}\Big|_{s=0}$$

$$=-i\hat{\omega}N_j(\tau)+N_j(\tau)i\hat{\omega}-\dot{N}_j(\tau) ,$$

so that by (4.6),

$$i\hat{\omega}N_j(\hat{\omega})=N_j(0)-N_j'(\hat{\omega}) .$$

We now introduce the recursive relations

$$M_j(t,\tau)=N_{j+1}(t,\tau)+\int_0^\tau ds\, M_j(t,s)N_{j+1}(s,\tau) ,$$

which imply

$$N_j'(\hat{\omega})=N_j'(0)\frac{1}{i\hat{\omega}-i\hat{\omega}N_{j+1}(\hat{\omega})}$$

$$=N_j'(0)\frac{1}{i\hat{\omega}-N_{j+1}(0)+N_{j+1}'(\hat{\omega})} .$$

We can now build a continued-fraction expansion for any quantity $A(\omega)$ by writing

$$A(\omega)\equiv N_0'(\hat{\omega})=A(0)\left[1\Big/\Big(i\hat{\omega}-N_1(0)+N_1'(0)\right.$$

$$\times\frac{1}{i\hat{\omega}-N_2(0)+N_2'(0)\,(1/\ldots)}\Big)\Big]\,.$$

When applied to the case that $A(\omega)$ is a correlation function, this is entirely equivalent to Mori's continued-fraction expansion.[5(b)]

APPENDIX D: EQUATION $M=N+M*N$

Let us consider the equation[20]

$$\begin{aligned} M(t,\tau) &= N(t,\tau)+M*N(t,\tau) \\ &= N(t,\tau)+\int ds\, M(t,s)N(s,\tau)\,. \end{aligned} \tag{D1}$$

Because of the associativity of the convolution product, we can immediately write the expression of M in terms of N implied by (D1), namely,

$$M(t,\tau)=\sum_{k=1}^{\infty} N^{*k}(t,\tau)\,, \tag{D2}$$

where $N^{*k}=N*N*\cdots*N$ (k factors N) is the kth convolution power of N (we verify that $M=\sum N^{*k}=N+\sum N^{*k}*N=N+M*N$). Formula (D2) implies the commutation relation

$$M*N=\sum_{k=2}^{\infty} N^{*k}=N*M\,,$$

which implies in turn that Eq. (D1) is perfectly symmetric in M and $-N$, that is, (D1) is unaltered if M and $-N$ are interchanged; thus, expressions of N in terms of M may be obtained by simply interchanging M with $-N$ in expressions of M in terms of N. Hence, it follows from (D2) that

$$-N=\sum_{k=1}^{\infty}(-M)^{*k}\,. \tag{D3}$$

If $M(t,\tau)$ vanishes when $\tau-t<0$, then (D1) implies that $N(t,\tau)$ also vanishes when $\tau-t<0$. Indeed, it is readily verified that if $A(t,\tau)$ and $B(t,\tau)$ vanish when $\tau-t<0$, then the same holds for $A*B(t,\tau)=\int_t^\tau ds\,A(t,s)B(s,\tau)$, from which it immediately follows, by the associativity of the convolution product, that if $M(t,\tau)$ vanishes when $\tau-t<0$, then so does $N(t,\tau)$ as given by (D3).

Equation (D1) also has the following implication: If $M(t,\tau)$ has the time-translation property

$$M(t,\tau)=e^{i\theta L}M(t-\theta,\tau-\theta)\,e^{-i\theta L}\,, \tag{D4}$$

where L is some operator, then $N(t,\tau)$ also has the same property. We first verify that if $A(t,\tau)$ and $B(t,\tau)$ have property (D4), then so does $A*B(t,\tau)$: Indeed,

$$\begin{aligned} A*B(t,\tau) &= \int ds\, e^{i\theta L}A(t-\theta,s-\theta)e^{-i\theta L} \\ &\quad\times e^{i\theta L}B(s-\theta,\tau-\theta)e^{-i\theta L} \\ &= e^{i\theta L}A*B(t-\theta,\tau-\theta)e^{-i\theta L}\;; \end{aligned}$$

the above implies, by the associativity of the convolution product, that if M satisfies (D4), then so does N as given by (D3).

Let us now introduce Fourier transforms defined as follows:

$$A(\hat{\omega})\equiv\int d\tau\,A(0,\tau)e^{-i\hat{\omega}\tau}\,, \tag{D5}$$

where

$$\hat{\omega}\equiv\omega-L\,.$$

If $M(t,\tau)$ satisfies (D4), we have by the results (A6)–(A8) of Appendix A that the Fourier transform of Eq. (D1) is

$$M(\hat{\omega})=N(\hat{\omega})+M(\hat{\omega})N(\hat{\omega})\,, \tag{D6}$$

or equivalently,

$$N(\hat{\omega})=M(\hat{\omega})/[1+M(\hat{\omega})]=-\sum_{k=1}^{\infty}[-M(\hat{\omega})]^k\,, \tag{D7}$$

this being of course the Fourier transform of (D3).

We now restrict ourselves to the case that $M(t,\tau)$, and therefore also $N(t,\tau)$, vanishes when $\tau-t<0$; Eq. (D1) can then be written

$$M(t,\tau)=N(t,\tau)+\int_t^\tau ds\,M(t,s)N(s,\tau)\,. \tag{D8}$$

In order to write the expression of M in terms of N in a form that is practical for physical discussion, we define an operator Λ as follows: When appearing inside a product of double-time operators $A_i(t_i,\tau_i)$, Λ makes *all* the t_i's on its *right*-hand side which are *smaller than, equal to* the *largest* τ_i on its *left*-hand side. For instance, if $t_i<s$, $i=1,2,3$, then

$$A(t_1,s)\Lambda B(t_2,\tau_2)C(t_3,\tau_3)=A(t_1,s)B(s,\tau_2)\,C(s,\tau_3)\,.$$

We can now write Eq. (D8) as

$$M(t,\tau)=N(t,\tau)+\int_t^\tau ds\,M(t,s)\,\Lambda N(t,\tau)\,,$$

which has the solution

$$M(t,\tau)=\frac{d}{d\tau}\exp_{\rightarrow}\Big[\int_t^\tau ds\,\Lambda N(t,s)\Big]\;; \tag{D9}$$

this follows from the fact that if $F(\tau)=\exp_{\rightarrow}[\int_t^\tau ds\,G(s)]$, then

$$\dot{F}(\tau)=F(\tau)G(\tau)=\Big[1+\int_t^\tau ds\,\dot{F}(s)\Big]\,G(\tau)\,.$$

We give explicitly the term of third order in N in (D9): It is

$$\begin{aligned} &\int_t^\tau ds\int_t^s ds'\,\Lambda N(t,s')\Lambda N(t,s)\Lambda N(t,\tau) \\ &\qquad=\int_t^\tau ds\int_t^s ds'\,N(t,s')N(s',s)N(s,\tau)\,. \end{aligned}$$

One readily verifies the identity of (D9) and (D2) by referring to formula (A4).

Let us now assume that M is of the form

$$\begin{aligned} M(t,\tau) &= \frac{d}{d\tau}\exp_{\rightarrow}\Big[\int_t^\tau ds\,m(t,s)\Big]P \\ &= \exp_{\rightarrow}\Big[\int_t^\tau ds\,m(t,s)\Big]\,m(t,\tau)P\,, \end{aligned} \tag{D10}$$

where P is a (projection) operator acting on the left-hand side. We shall show that

$$N(t,\tau)=\exp_{\to}\left[\int_t^\tau ds\, m(t,s)\,(1-P\Lambda)\right] m(t,\tau)P \tag{D11}$$

satisfies Eq. (D8).

Proof: Introduce some time $\theta<t$, and define

$$M_\theta(t,\tau)\equiv\exp_{\to}\left[\int_t^\tau ds\, m(\theta,s)\right] m(\theta,\tau)Q\ , \tag{D12}$$

where

$$Q\equiv P\Lambda\ .$$

Applying the results of Appendix C, we have that

$$N_\theta(t,\tau)\equiv\exp_{\to}\left[\int_t^\tau ds\, m(\theta,s)\,(1-Q)\right] m(\theta,\tau)Q \tag{D13}$$

satisfies the equation

$$M_\theta(t,\tau)=N_\theta(t,\tau)+\int_t^\tau ds\, M_\theta(t,s)N_\theta(s,\tau)\quad . \tag{D14}$$

[In the above, $m(\theta,\ s)$ is considered a function of s alone, and it plays the role of $V(s)$ in Appendix C.] Now,

$$\begin{aligned} M_\theta(t,s)N_\theta(s,\tau)&=\exp_{\to}\left[\int_t^s ds'\, m(\theta,s')\right] m(\theta,s)P\Lambda\\ &\quad\times\exp_{\to}\left[\int_s^{\tau} ds'\, m(\theta,s')\,(1-P\Lambda)\right] m(\theta,\tau)P\Lambda\\ &=\exp_{\to}\left[\int_t^s ds'\, m(\theta,s')\right] m(\theta,s)P\\ &\quad\times\exp_{\to}\left[\int_s^\tau ds'\, m(s,s')\,(1-P\Lambda)\right] m(s,\tau)P\\ &=M_\theta(t,s)\Lambda^{-1}N(s,\ \tau)\ , \end{aligned} \tag{D15}$$

where $N(t,\ \tau)$ is given by (D11). Putting $\theta=t$ in Eq. (D14), and making use of (D15), we recover Eq. (D8) after identifying $M_t(t,\ \tau)\Lambda^{-1}$ with $M(t,\ \tau)$. This completes the proof.

We notice that had we taken $Q=P$ instead of $Q=P\Lambda$ in definition (D12), we would not have been able to get rid of the θ dependence of $N_\theta(s,\ \tau)$ in Eq. (D14). We would then have the equation

$$M(t,\tau)=N_t(t,\tau)+\int_t^\tau ds\, M(t,s)N_t(s,\tau)\ , \tag{D16}$$

where $N_t(s,\ \tau)$ is given by (D13) with $Q\to P$. If we let

$$m(t,\tau)=\sum{}^{(\mathrm{irr})}\, i m_\Gamma(t,\tau)\ ,$$

so that $M(t,\ \tau)$ is given by (5.9), we obtain for $N_\theta(t,\ \tau)$ a quantity whose density expansion has the same asymptotic behavior[21] as that of $N(t,\ \tau)$; but the dependence of $N_t(s,\ \tau)$ on *three* time arguments prevents the Fourier transform of (D16) from yielding simple or useful expressions, such as (D6) We have here an example of a quantity having a density expansion that can be truncated, but whose relation to M is not convenient for practical use.

APPENDIX E: WING BEHAVIOR OF SPECTRUM

The spectrum can be written

$$\begin{aligned} I(\omega)&=\mathrm{Tr}_s D\sigma U(\omega)D\\ &=\{D\,|\,\sigma U(\omega)\,|\,D\}\ , \end{aligned} \tag{E1}$$

where $\{\ |$ and $|\ \}$ denote, respectively, bras and kets in Liouville space (the notation $|\ \rangle\!\rangle$ is more commonly used). For any operators $A,\ B,\ \ldots\ ,$ we define

$$\mathrm{Re}A\equiv\tfrac{1}{2}(A+A^\dagger)\ ,$$

$$\mathrm{Im}A\equiv(1/2i)\,(A-A^\dagger)\ ,$$

where $A^\dagger$ denotes the Hermitian conjugate of A. We have the relations

$$\mathrm{Re}A=\mathrm{Re}A^\dagger\ ,\qquad \mathrm{Im}A=-\mathrm{Im}A^\dagger\ ,$$

$$\mathrm{Re}\{D|A|D\}=\{D|\mathrm{Re}A|D\}\ ,\quad \mathrm{Im}\{D|A|D\}=\{D|\mathrm{Im}A|D\}\ ,$$

$$\mathrm{Re}BAB^\dagger=B(\mathrm{Re}A)B^\dagger\ ,\qquad \mathrm{Im}BAB^\dagger=B(\mathrm{Im}A)B^\dagger\ .$$

Inserting $1=U(\omega)^\dagger[U(\omega)^\dagger]^{-1}$ in (E1), we write, using Eqs. (4.2) and (4.4),

$$I(\omega)=\frac{1}{i}\left\{D\left|\frac{1}{\hat\omega-C(\omega)^\dagger}\,[\hat\omega-C(\omega)^\dagger]\,\sigma\,\frac{1}{\hat\omega-C(\omega)}\right|D\right\} \tag{E2}$$

and deduce

$$\mathrm{Re}I(\omega)=\left\{D\left|\frac{1}{\hat\omega-C(\omega)^\dagger}[\mathrm{Im}\sigma C(\omega)]\,\frac{1}{\hat\omega-C(\omega)}\right|D\right\}\ , \tag{E3}$$

$$\mathrm{Im}I(\omega)=\left\{D\left|\frac{1}{\hat\omega-C(\omega)^\dagger}\,[\sigma\hat\omega-\mathrm{Re}\sigma C(\omega)]\,\frac{1}{\hat\omega-C(\omega)}\right|D\right\}. \tag{E4}$$

(Note that σ is a function of H_s, by Appendix C of Ref. 1, so that $\sigma\hat\omega$ is Hermitian.)

In the wings, at frequencies far from all eigenfrequencies of $H_s^\times$ and such that $|\hat\omega|\gg|C(\omega)|$, we have

$$I(\omega)\to\{D|\,(1/\hat\omega)\,[\mathrm{Im}\sigma C(\omega)]\,(1/\hat\omega)\,|D\}+i\{D|\,\sigma/\hat\omega\,|D\}\ . \tag{E5}$$

[Here we assume that the translational motion of the radiator is neglected, or that it has been included in the "bath" (cf. Sec. VIII of Ref. 1), so that the spectrum of $H_s^\times$ is discrete.]

We now show that if $C(\omega)$ is treated to first order in the density, the line shape $\mathrm{Re}I(\omega)$ is, in the wings, proportional to the one-perturber line shape $\mathrm{Re}I_1(\omega)$, where $I_1(\omega)$ is the spectrum corresponding to the presence of only one perturbing atom. We have

$$\begin{aligned} I_1(\omega)&\equiv\mathfrak{F}\left\{\mathrm{Tr}_{sj}De^{-\beta H_{sj}}\,e^{i\tau H_{sj}^\times}D\right\}(\mathrm{Tr}_{sj}e^{-\beta H_{sj}})^{-1}\\ &\propto\mathrm{Tr}_s D\rho_s\,\mathcal{J}(\hat\omega)D\ , \end{aligned}$$

where

$$\mathcal{J}(\tau)\equiv(n\mathcal{V}/Z_j)e^{\beta H_s}\,(\mathrm{Tr}_j\,e^{-\beta H_{sj}}e^{i\tau H_{sj}^\times})\,e^{-i\tau H_s^\times}\ .$$

According to (3.23) and (4.12),

$$\dot{\mathcal{J}}(\tau)=iR^{(1)}(-i\beta,\tau)=N^{(1)}(\tau)\ ,$$

so that by (4.6),

$$N^{(1)}(\hat\omega)=\dot{\mathcal{J}}(\hat\omega)=-\mathcal{J}(\tau=0)+\mathcal{J}(\hat\omega)i\hat\omega\ .$$

With the approximation $N \rightarrow N^{(1)}$, $\sigma \rightarrow \rho_s$, the real part of (E5) becomes [recall $C(\omega) = \hat{\omega} N(\hat{\omega})$]

$$\begin{aligned} \mathrm{Re} I(\omega) &= \{D \,|\, \mathrm{Im} \rho_s (1/\hat{\omega}) C^{(1)}(\omega)\, (1/\hat{\omega}) \,|\, D\} \\ &= \{D \,|\, \mathrm{Re} \rho_s\, J(\hat{\omega}) \,|\, D\} \\ &\propto \mathrm{Re} I_1(\omega) \end{aligned}$$

[note that $J(\tau = 0) = n \mathcal{V} (e^{\beta H_s}/Z_j)\, \mathrm{Tr}_j e^{-\beta H_{sj}}$ is Hermitian, so that the term $\mathrm{Im} J(\tau = 0) = 0$].

Note added in proof. After completion of this work, the author became aware of the vast amount of literature dealing with the density expansion of transport coefficients (Ref. 22) in which expansions analogous to those given here or in Ref. 1 are performed; Albers and Oppenheim (Ref. 23) have also applied these methods to the specific case of pressure broadening. In Ref. 1, it was argued that each term $R^{(k)}(t)$ in the density expansion $R = \sum n^k R^{(k)}$ tends to a constant as $t \rightarrow \infty$; in fact, this can be shown rigorously (Ref. 24) only for the terms $R^{(1)}$ and $R^{(2)}$. It appears that recollision cycles cause the higher-order terms to grow indefinitely with time (Refs. 23 and 25) [though unanimity has not yet been reached concerning the form (Ref. 26) or even existence (Ref. 27) of these secularities]. Thus, the discussion given in Sec. VII of Ref. 1 only shows that the density expansion of $R(t)$ is free of the "worst" divergences present in the expansion of $U(t)$, namely, those arising from successions of uncorrelated collisions of the radiator with clusters of perturbers. Even though the terms $R^{(k)}(t)$, $k \geq 3$, grow with time, it is still believed that $R(t)$ itself exists in the limit $t \rightarrow \infty$, so that one is still justified in approximating $R(t)$ by $nR^{(1)}(t)$ or $nR^{(1)} + n^2 R^{(2)}$, which also exist as $t \rightarrow \infty$. In order to get approximations of higher order in the density, resummation procedures have been proposed (Refs. 23 and 28), but these still do not seem to eliminate all divergences (Ref. 29). The author acknowledges discussions with Professor S. Fujita and Professor B. C. Eu on these matters.

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[7] See Appendix B of Ref. 1 or references therein for the definition of the symmetry number $\sigma(\Gamma)$.

[8] See Appendix A of Ref. 1 or references therein for a discussion of cumulants. The cumulants used here are $c \rightarrow$ cumulants as defined in Ref. 1, but we omit writing the arrows ($\rightarrow$) for simplicity.

[9] We shall write reduced-density expansions indifferently as $\sum n^k R^{(k)}$ or as $\sum R^{(k)}$, it being understood that when n^k does not appear, it is included in $R^{(k)}$.

[10] In Sec. VII of Ref. 1, the operator $m_\Gamma^t(\tau)$ equals the operator $m_\Gamma(-i\beta + \tau - t, \tau)$ of this paper. The two time arguments in $m_\Gamma(-i\beta + t, \tau)$ indicate the times at which the interactions are turned on and off, respectively; in $m_\Gamma^t(\tau)$, τ is the time at which the interactions are turned off, while t says since how long they have been turned on.

[11] Note that $(1/\hat{\omega})^k * (\omega - \omega_b)^{-1} = (\hat{\omega} - \omega_b)^k$; thus, in the third term of (3.35), for instance, the component $(\bar{R}/i\omega)$ of $R(\omega)$ yields a term $(1/\hat{\omega})\bar{R}(1/\hat{\omega})\bar{R}(1/\hat{\omega})$ which is of third order in $(1/\hat{\omega})$. Note that poles of $R(\omega)$ at bound-spectrum frequencies $\omega_b \neq 0$ cause no problem, for if we set $R(\omega) \rightarrow R_b/(\omega - \omega_b)$ in the third term of (3.35), for instance, we get $[[(\hat{\omega} - \omega_b)^{-1} R_b (1/\hat{\omega})] * R_b/(\omega - \omega_b)](1/\hat{\omega}) = (\hat{\omega} - 2\omega_b)^{-1} R_b \times (\hat{\omega} - \omega_b)^{-1} R_b (1/\hat{\omega})$ which still has poles of only order 1.

[12] In Ref. 6, a well-behaved "density expansion" of the spectrum was also obtained (this is not a strict density expansion, since the coefficients of powers of the density themselves depend on the density); this was achieved by separating the adiabatic equivalent of $\int_0^\tau dt\, R(t) \equiv g(\tau)$ into a *locally averaged* part and an oscillating part. The method of the present paper, which separates $R(t)$ into a *fully averaged* part $\bar{R}$ and an oscillating part $\tilde{R}$ is simpler and physically more meaningful (applying the local averaging method to the general nonadiabatic theory considered here leads to expressions too complicated to be of any practical or informative value).

[13] For discussions of fine structure in the wings of spectral lines, see, for instance, Ref. 6 and references therein; also, A. Royer, Phys. Rev. A 4, 499 (1971), and references therein.

[14] See the last paragraph of Sec. IV of Ref. 6.

[15] Had we chosen to write $iB(\hat{\omega}) = [\hat{\omega} - C_1(\omega)]^{-1}$ instead of (4.4), we would have $M_1(\hat{\omega}) = \dot{B}(\hat{\omega}) + [B(0) - 1]$ instead of (4.7), which would complicate the discussion. [Note that $B(0) \neq 1$ unless initial correlations are neglected, and recall that $U_I(\tau) = B(0)^{-1} B(\tau)$.] We can still write $B(\hat{\omega})$ in resolvent form, but starting from the equivalent form for $U_I(\hat{\omega})$, as done in Eq. (4.17).

[16] The operator $\langle M_c(\omega) \rangle$ introduced by Fano (Ref. 3) is equal to our $\hat{\omega} N(\hat{\omega})$ (with the difference that Fano neglects initial correlations between atoms); also, Fano's operator $\langle M(\omega) \rangle$, which is also defined in Sec. III of Ref. 1, corresponds to our $\hat{\omega} M(\hat{\omega})$.

[17] We also define $F(\hat{\omega}_{\rightarrow}) \equiv \int_0^\infty d\tau F(\tau) e^{-i\hat{\omega}\tau} = F(\omega) * (1/i\hat{\omega})$; for simplicity, we neglect writing the arrow in this case, setting $F(\hat{\omega}_{\rightarrow}) \equiv F(\hat{\omega})$, as according to (4.3).

[18] We note that the interactions between sets of particles are "turned on" at complex times $-i\beta + s$, so that the interactions taking place between "times" $-i\beta + s$ and s build up correlations between the particles at the *physical* turning-on time s. In other words, when the interactions are turned on, Boltzmann factors are also turned on, which discriminate against states of the particles which could not have been reached if the interactions had been acting since long before time s. If this were not the case, one might get infinite energies, for evolving without mutual interaction particles may get arbitrarily close to each other, which may imply arbitrarily large potential

energies if the interactions are suddenly turned on.

[19] If initial correlations between particles are neglected, there is no advantage in expressing L_2(i.e., N) in terms of the $R^{(k)}$'s [cf. Eq. (5.10)]; on the other hand, when initial correlations are included, it is hard to see the structure of L_2 if one does not make use of the $R^{(k)}$'s.

[20] Note that the more general equation $M = N + \lambda M * N$ is obtained from (D1) by the transformation $M \rightarrow \lambda M$, $N \rightarrow \lambda N$, so that its solutions are obtained from those of (D1) by the same transformation.

[21] This is because if two successive collision times τ_i and τ_{i+1} in a product such as $\Pi_j m_{\Gamma_j}(\theta, \tau_j)$, $\theta < \tau_1 \le \tau_2 \le \tau_3 \ldots$, are separated by more than the maximum collision duration $t_{\max} \equiv \max\{t_{\Gamma_j}\}$, then the operators m_{Γ_j} separate into two time-disentangled groups, and the average $\langle\ \rangle$ of their product factorizes: $\langle \Pi_j m_{\Gamma_j} \rangle \rightarrow \langle \Pi_{j \le i} m_{\Gamma_j} \rangle \langle \Pi_{j > i} m_{\Gamma_j} \rangle$. Now, the general term in $N_\theta(t, \tau)$ is of the form (5.6), with the correspondence $A_i(t, s_i) \rightarrow m_{\Gamma_i}(\theta, s_i)$ and $\Lambda \rightarrow P$; if for some i, $(s_{i+1} - s_i) > t_{\max}$, then the operator P appearing between m_{Γ_i} and $m_{\Gamma_{i+1}}$ has the same effect as the operator 1, which implies that the first two order terms in the density expansion of $N_\theta(t, \tau)$ exist in the limit $t \rightarrow -\infty$, by the same type of argument as those following Eq. (5.6).

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PHYSICAL REVIEW A VOLUME 7, NUMBER 3 MARCH 1973

Simulation of Diatomic Homonuclear Liquids

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(Received 21 August 1972)

The molecular-dynamic method was used to simulate a fluid of 500 rigid diatomic homonuclear molecules interacting by a double Lennard–Jones potential. The equilibrium and time-dependent properties are calculated in the liquid phase. The computed pressure and the internal energy agree quantitatively to a few percent with experimental values for nitrogen. The reorientational and the velocity of the center-of-gravity self-correlation functions are also discussed. The memory-function formalism and the extended-diffusion models are used to interpret the reorientational self-correlation functions. The analysis reveals that these self-correlation functions have an exponential behavior for times larger than 5×10^{-13} sec. In this model, considering present computing precision, there is no observable hydrodynamic-type relaxation in the reorientational self-correlation functions.

I. INTRODUCTION

The molecular-dynamic (MD) method has been widely used to study the monoatomic fluids.[1-3] Recent computer experiments, considering a Lennard–Jones (LJ) potential as the interaction between pairs of particles have lead to a determination of several thermodynamic properties (pressure, internal energy, and phase transition[4]), the equilibrium correlation functions,[5] the self-correlation function of the velocities, and the self-diffusion coefficients.[6] For argon, the calculated quantities agree within a few percent with the experimental data. The purpose of this comparison between computed and experimental values is not to demonstrate that the real potential is a LJ potential (for instance in argon), but to establish that the proposed model has all the significant physical properties of a real system. Then the simulated system can be considered as a reference for theoretical studies of equilibrium and transport properties.

Up to the present time very few MD results on polyatomic liquids have been obtained, mainly because the molecular interactions are badly known. To our knowledge, the only MD calculations on polyatomic fluids have been carried out by Harp and Berne[7] using a Stockmayer-type potential to simulate CO and N_2 and by Rahman and Stillinger[8] to simulate H_2O.

In this work, we study another type of interaction potential, the so-called diatomic potential.[9] This potential has been successfully used to determine