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Stochastic Aspects in the Theory of Spectral-Line Broadening. I. Collision Time Statistics and N-Perturber Limit[1]

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An atom in a gas or plasma experiences a random potential which gives rise to the so-called pressure broadening. The corresponding line shape is obtained in the usual two-level model by a trace operation from the Fourier transform of $\langle T(t,0)\rangle$, the average of the time-development operator. Under certain technical assumptions it is rigorously shown by probabilistic techniques that $\langle T(t,0)\rangle$ falls off faster than $t^{-3+\epsilon}$ for any $\epsilon > 0$, giving a continuous Fourier transform and line shape. An alternative expression is derived for the latter which explicitly displays its positivity and which is a limit over increasing perturber numbers. The latter generalizes results of von Waldenfels. Part I is preparatory for Part II, where a noncommutative cluster expansion is applied to the line-shape problem. Several open questions are pointed out which merit a rigorous investigation.

KEY WORDS: Pressure broadening; stochastic differential equations; asymptotic decay; N-particle limit.

1. INTRODUCTION. THE MODEL. NOTATION

When one places an atom with Hamiltonian H_A in a gas or plasma the atom's electrons will experience an additional rapidly varying perturbing potential $V_P(t)$, due to the Coulomb potentials of the gas or plasma particles (perturbers). If one treats the perturbers as classical point particles, the potential $V_P(t)$ depends on the configuration of the perturbers, e.g., on their positions and velocities at time $t = 0$. Describing the gas or plasma by

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a statistical ensemble, $V_P(t)$ becomes a *random* potential, and the total Hamiltonian is

$$H(t) = H_A + V_P(t) \tag{1.1}$$

A spectral line emitted by atoms in a gas or plasma will be broadened and deformed. This has two reasons, first the Doppler shift caused by the atoms' thermal motion, and second the effect of the perturbing potential V_P. It is customary to calculate the broadening for an atom at rest and then essentially to convolute with the Doppler broadening; cf. Ref. 1 for a review of the subject and a collection of references. It should be pointed out, however, that the situation is more complicated because the potential V_P also depends on the atom's velocity.[2] In the present paper we consider the case of an atom at rest.

In the general formula for the line-shape function the time-development operator $T_H(t, 0)$ for the time-dependent Hamiltonian H enters. It satisfies the Schrödinger equation

$$\dot{T}_H(t,0) = -(i/\hbar)\left[H_A + V_P(t)\right]T_H(t,0) \tag{1.2}$$

which is now a *stochastic* differential equation.

Its solution is a complicated time-ordered exponential. Although V_P is a simple sum of individual perturber potentials, $T_H(t,0)$ does not factorize into factors originating from individual perturbers. In the interaction picture with respect to H_A this is seen to be due to the noncommutativity of the resulting potentials at different times. Averages or expectations are therefore difficult to perform, even if one treats the perturbers as an ideal gas, in the plasma case with suitable shielding, as will be done here. The statistics of an ideal gas can be described by the Maxwell distribution for the velocities and either by a uniform distribution of the positions or by a distribution of the time and position of closest approach ("collision" or "arrival" times and "impact parameters"). The collision times form a Poisson process. This was first exploited systematically by von Waldenfels.[3] The present paper also uses collision time techniques. They are nonstandard in this field.

The atom will be idealized to a two-level system, possibly degenerate. This is a standard approximation and it seems to be fairly realistic, as explained below. The two energy levels are of course those associated to the spectral line in question. The perturbing potentials for this idealized situation are obtained from V_P essentially by a projection. Then the Schrödinger equation becomes a *finite-dimensional stochastic operator equation* for a time-development operator $T(t, t')$.

The line-shape problem then essentially consists in solving a stochastic Schrödinger operator equation for a time-development operator and in determining its expectation. Subsequent Fourier transformation with respect to time with a certain trace operation will yield the line-shape function. The Fourier transform involved makes it clear that one cannot take just a few terms of the Dyson series for the time-ordered exponential because that would be a good approximation for small times only.

There are many interesting open questions connected with this problem, some more practical and some more theoretical–mathematical. We mention a few of the latter.

(i) How fast does the expectation of the time-development operator decrease when time goes to infinity? How smooth is its Fourier transform (and hence the line shape)?

(ii) Is there a convergent series expansion of the line-shape function?

(iii) Are there rigorous (and possibly also useful) estimates for the asymptotics of the Fourier transform (and thus of the line shape)?

(iv) Are there rigorous estimates for the line center and the linewidth?

(v) How will Doppler broadening affect such rigorous results?

This paper contributes only modestly to the solution of these problems. It is rather intended as a stimulant for further research. Question (i) is considered in Section 2 of this paper. Under certain technical conditions it is shown that the expectation of the time-development operator decays faster than $|t|^{-3+\epsilon}$ for any $\epsilon > 0$ and thus is L^1. This implies that its Fourier transform and the line-shape function are continuous and vanish at ∞. This is physically reasonable; but it is also important technical information to be used later. These fall-off results are the first of their kind. They merit further investigation and extension.

In Section 3 we derive an equivalent expression for the Fourier transform of $\langle T(t,0)\rangle$ which exhibits the positivity properties explicitly. We show that it can be written as a limit over increasing perturber numbers where we generalize previous results.[3,4] In particular, if $\langle T(\cdot,0)\rangle \in L^1$ then the convergence is uniform in ω. Furthermore, an external time-independent potential is incorporated. This allows us to treat the ions quasistatically. Interesting mathematical problems arise with the replacement of an upper integration limit by a random variable (Proposition 2.1). The main result of this section, Theorem 3.1, is an extension of a result in Refs. 3 and 4, the precise relationship being explained at the beginning of Section 3. This Theorem will be basic for Part II.

In Part II of this paper question (ii) on a series expansion for the line-shape function is attacked. We generalize an approach of von Waldenfels[3] to include static ions. Previously, only a single particle species was covered. Generalizing ideas of Ref. 3 we develop a noncommutative cluster expansion in terms of truncated operator functions which are related to the Mayer–Ursell functions of statistical mechanics and to the truncated n-point functions of quantum field theory. A direct "physical" derivation of the first-order term has been given by us in Ref. 5; it is shown that the first order partially contains the overlapping of the perturber potentials. A numerical evaluation for Lyman-α gives good agreement with experiment on the line wings and deviations in the line center, presumably due to the quasistatic treatment of the ions.

The approach is also generalized to include moving ions. However, it is unclear at the moment how good the first-order approximation is in this case.

As for rigorous estimates for the asymptotics of the line-shape function [problem (iii)], partial results have recently been obtained by us.[6] It was shown within the line-space model (see below) that the sixth moment of the line-shape function exists while the eighth moment does not. This indicates an asymptotic fall-off faster than ω^{-7} but not faster than ω^{-9}.

Rigorous estimates for the linewidth and line center [problem (iv)] are not known, but they would be of great relevance because recent linewidth measurement of Grützmacher and Wende[7] are in disagreement with calculations based on static ions by about a factor of 2.4. Good results are given by calculations with the method of model microfields (MMM),[8] but it should be pointed out that this is not a microscopic but a phenomenological theory, which simulates the stochastic behavior of the perturbing potential. There are several other attempts to incorporate ion-dynamical effects: cf. Ref. 9 for references and criticism.

Doppler broadening complicates the whole picture [problem (v)]. There are Monte Carlo calculations[10] which indicate that the use of the reduced mass of the ion-radiator system with a convolution by the ordinary Doppler profile may be a good approximation. Analytically nothing rigorous seems to be known about this.

The Model in Line Space

Throughout we use units in which

$$\hbar = 1$$

Consider an optical transition from an atomic energy level E_{in} to E_{fin}. Let $\mathscr{H}_{\text{in}}$ and $\mathscr{H}_{\text{fin}}$ be the associated eigenspaces with orthonormal bases $\{|i\rangle\}$, $\{|f\rangle\}$. Let

$$\omega_0 = E_{\text{in}} - E_{\text{fin}}$$

and let $\mathbf{X}$ be the position operator of the radiating electron (or, if several electrons are involved, their sum). If $L(\omega)$ denotes the normalized line-shape function, $\int L\, d\omega = 1$, then dipole radiation gives[1]

$$L(\omega) = (2\pi)^{-1} A \int dt\, e^{i\omega t} \times \sum_{ifi'f'} \langle\langle i|\mathbf{X}|f\rangle\langle f|T_H(t,0)^*|f'\rangle\langle f'|\mathbf{X}|i'\rangle\langle i'|T_H(t,0)|i\rangle\rangle_{\text{av}} \quad (1.3)$$

where A is a normalization constant,

$$A^{-1} = \sum_{if} |\langle i|\mathbf{X}|f\rangle|^2$$

and where $\langle\ \rangle_{\text{av}}$ denotes expectation, i.e., averaging over perturber configurations. Note that for $V_P = 0$ one obtains

$$L(\omega) = \delta(\omega - \omega_0)$$

It is now convenient to introduce the *line space* of Baranger[10,1]

$$\mathscr{H} = \mathscr{H}_{\text{in}} \otimes \mathscr{H}_{\text{fin}} \tag{1.4}$$

and to define operators $D, V(t), T(t,t')$ in $\mathscr{H}$ by

$$\begin{aligned}
\langle if|D|i'f'\rangle &:= A\langle i|\mathbf{X}|f\rangle\langle f'|\mathbf{X}|i'\rangle \\
\langle if|V(t)|i'f'\rangle &:= \langle i|V_P(t)|i'\rangle\delta_{ff'} - \delta_{ii'}\langle f'|V_P(t)|f\rangle \\
\langle if|T(t,t')|i'f'\rangle &:= \langle i|T_H(t,t')|i'\rangle\langle f'|T_H(t,t')^*|f\rangle e^{i\omega_0(t-t')}
\end{aligned} \tag{1.5}$$

It is easy to show that D is positive definite. A simple calculation shows that $L(\omega)$ is given by

$$L(\omega) = (2\pi)^{-1}\int dt\, e^{i(\omega-\omega_0)t}\mathrm{Tr}\langle DT(t,0)\rangle_{\text{av}} \tag{1.6}$$

It was pointed out by us[6] that $\mathrm{Tr}\langle DT(t,0)\rangle_{\text{av}}$ is a positive-definite function of t so that by Bochner's theorem it is the Fourier transform of a positive measure. Note that although the definitions in Eq. (1.5) are basis dependent the formula in Eq. (1.6) is not.

One usually makes the nonquenching assumption[1] according to which one can neglect transitions caused by the perturbers. This means that

$$\langle i|V_P|f\rangle$$

is approximated by 0. Then a straightforward calculation shows that T satisfies

$$\dot{T}(t,t') = iV(t)T(t,t') \tag{1.7}$$

This Schrödinger equation is again a stochastic differential equation. If shielding is taken into account by a cutoff at the Debye sphere, $V(t)$ has discontinuities, but with probability one only finitely many in each bounded time interval. At such points Eq. (1.7) is not defined. One may consider the corresponding integral equation

$$T(t,t') = \mathbb{1} - i\int_{t'}^{t} ds\, V(s)T(s,t') \tag{1.8}$$

We consider a plasma of ions and electrons treated as an ideal gas with a charge shielding by a simple cutoff at the Debye radius ρ_D so that a perturber contributes a Coulomb potential or zero to V_P depending on whether it is inside the Debye sphere or not. If $\mathbf{r}_\kappa(t)$ is the position of the

κth perturber of charge $\pm e$, its contribution to V_P is thus

$$\mp e^2|\mathbf{X} - \mathbf{r}_\kappa(t)|^{-1}\theta(\rho_D - r_\kappa(t)) \tag{1.9}$$

in case of a one-electron atom. Perturbing electrons are taken to move on straight lines. With $\mathbf{v}_\kappa$ the velocity, τ_κ the collision time (time of closest approach), and $\boldsymbol{\rho}_\kappa$ the impact parameter $[\boldsymbol{\rho}_\kappa = \mathbf{r}_\kappa(\tau_\kappa)]$ one has

$$\mathbf{r}_\kappa(t) = \boldsymbol{\rho}_\kappa + \mathbf{v}_\kappa(t - \tau_\kappa) \tag{1.10}$$

Note that $\boldsymbol{\rho}_\kappa \perp \mathbf{v}_\kappa$. If the perturbing ions are taken to be at rest (quasistatic approximation) one has for them $\mathbf{r}_\kappa(t) \equiv \mathbf{r}_\kappa$.

We can express the one-perturber potential Eq. (1.9) in line space by the analog of Eq. (1.5). With Eq. (1.10) one obtains an expression of the form

$$\varphi(\boldsymbol{\rho}_\kappa ; \mathbf{v}_\kappa ; t - \tau_\kappa) \tag{1.11}$$

for the κth electron contribution to $V(t)$. One easily sees that φ is uniformly bounded.

$$\sup_{\boldsymbol{\rho},\mathbf{v},t} \|\varphi(\boldsymbol{\rho}, \mathbf{v}, t)\| < \infty \tag{1.12}$$

Collision-Time Statistics

This was first used in the present context by von Waldenfels,[3] and later by us[6] in connection with asymptotics of the line-shape function.

With probability 1, there is only a finite number of particles in the Debye sphere at a given time. One can therefore index the perturbers (electrons) according to their collision time. If $\kappa > 0$, the index κ refers to the κth particle colliding after $t = 0$; if $\kappa \leqslant 0$, it refers to the $(|\kappa| + 1)$st perturber colliding before $t = 0$.[4]

For an ideal gas the *interarrival* (or *intercollision*) *times*

$$u_\kappa := \tau_{\kappa+1} - \tau_\kappa \tag{1.13}$$

are independent random variables distributed exponentially according to

$$ce^{-cu}\,du \tag{1.14}$$

Here c is the *mean collision frequency*

$$c := \langle u_\kappa \rangle_{\text{av}}^{-1} = \pi \rho_D^2 \bar{v} \nu$$

[4] This procedure has to be modified if the shielding is in the form of a smooth Debye–Hückel potential since then the collision rate is infinite. In this case one may first consider a large sphere and then let its radius go to infinity.

and $\bar{v}$ and ν are mean velocity and density, respectively. The collision times form a stationary Poisson process.

The set of impact parameters and velocities $\{(\boldsymbol{\rho}_\kappa, \mathbf{v}_\kappa)\}$ are independent random variables which are identically distributed [according to

$$\tfrac{1}{2}(m/2k_B T\pi\rho_D)^2 v e^{-m_e v^2/2k_B T}\, d^2\rho\, d^3 v \tag{1.15}$$

where the factor v expresses the fact that the number of electrons entering the Debye sphere is proportional to their velocity v; the special form of Eq. (1.15) will not be needed in this paper].

Remark. If one has several moving-particle species the above formulation is changed only slightly. The perturbers get an additional parameter (charge, say). The collision times still form a Poisson process with the sum of the individual collision frequencies. The averaging is now also over the additional parameter.

Notation

In the following we consider the ions as static. The total potential in line space is then of the form

$$V(t) = V_i + V_e(t) \equiv V_i + \sum_\kappa \varphi(\boldsymbol{\rho}_\kappa, \mathbf{v}_\kappa; t - \tau_\kappa) \tag{1.16}$$

where $V_i = V_{\text{ions}}$, $V_e = V_{\text{electrons}}$. As a consequence the processes $V(t)$ and $V_e(t)$ are *stationary* so that, in particular,

$$\langle T(t+s, t'+s)\rangle_{\text{av}} = \langle T(t,t')\rangle_{\text{av}} \tag{1.17}$$

with similar relations for the correlation functions of the potential.

The expectation or averaging is decomposed into two steps, first over the electrons with a fixed ion configuration, then over ions. The electron expectation is written as $\langle\ \rangle$,

$$\langle\ \rangle := \langle\ \rangle_{\text{electrons}} \tag{1.18}$$

Then the total expectation is

$$\langle\ \rangle_{\text{av}} = \langle\langle\ \rangle\rangle_{\text{ions}} \tag{1.19}$$

We introduce the *intensity operator J_i for fixed ion configuration,*

$$J_i(\omega) := (2\pi)^{-1}\int dt\, e^{i\omega t}\langle T(t,0)\rangle \tag{1.20}$$

It is easy to see by stationarity that J_i defines a positive operator-valued measure.[6] From Eq. (1.6) one has

$$L(\omega) = \operatorname{Tr} D\langle J_i(\omega - \omega_0)\rangle_{\text{ions}} \tag{1.21}$$

The ion averaging can be performed with the Holtsmark distribution or a variant thereof.[1]

We will have to consider different time-development operators simultaneously. For the solution of a Schrödinger-type equation

$$\begin{aligned} \frac{d}{dt} U(t,t') &= -i\phi(t)U(t,t') \\ U(t',t') &= \mathbb{1} \end{aligned} \tag{1.22}$$

we therefore write

$$U(t,t') = U(t,t';\phi(\cdot)) \tag{1.23}$$

or

$$U(t,t') = U(t,t';\phi) \tag{1.24}$$

In this notation one has

$$T(t,t') = U(t,t';V)$$

Alternatively, one can use a continuous product notation (cf. Refs. 12, 3, 4).

The indicator function χ_S of a set S is given by

$$\chi_S(x) = \begin{cases} 1, & x \in S \\ 0, & x \notin S \end{cases} \tag{1.25}$$

Furthermore, ν and c denote mean density and collision frequency, respectively.

2. LARGE-t BEHAVIOR OF $\langle T(t,0)\rangle$

We are going to prove in Theorem 2.1 that under weak assumptions on the potential, $\langle T(t,0)\rangle$ falls off faster than $|t|^{-3+\epsilon}$ as $|t|\to\infty$, for any $\epsilon > 0$. One would expect an exponential falloff, and indeed we can prove this if one introduces a lower velocity cutoff in the Maxwell distribution. Throughout this section we use shielding in form of a cutoff at the Debye sphere.

Proposition 2.1. Consider $\langle T(t,0)\rangle$ for a fixed ion potential and for a modified Maxwell velocity distribution in which all velocities smaller than some $v_{\min}$ are excluded. If, for some $\rho^{(0)}$ and $\mathbf{v}^{(0)}$, the one-perturber (electron) S matrix in the ion-interaction picture does not have an eigenvalue 1, then $\|\langle T(t,0)\rangle\|$ falls off at least exponentially for large $|t|$.

Proof. We first consider the case that there is no ion potential and the case $t > 0$.

The existence of $v_{\min}$ implies that there is a maximal length of time, t_L, for a perturber to stay in the Debye sphere. Hence the individual one-perturber potentials are nonzero in a time interval of length at most t_L. To estimate $\|\langle T(t,0)\rangle\|$ we consider the time intervals $[-t_L,0],[0,t_L],[t_L, 2t_L],\ldots$ of length t_L plus a remainder $[nt_L,t]$ with $0 \leqslant t - nt_L < 5t_L$ and n a multiple of 5. We decompose $T(t,0)$ accordingly,

$$T(t,0) = T(t,nt_L)\prod_n^1 T(\nu t_L,(\nu-1)t_L) \equiv T(t,nt_L)\prod_n^1 T_\nu \tag{2.1}$$

Each operator T_ν depends only on perturbers colliding in the $(\nu-1)$st, νth and $(\nu+1)$st interval. Potential contributions from different intervals of equal length are independent and identically distributed.

We denote by $\langle\ \rangle_\nu$ the conditional expectation given the potential originating from all intervals except the νth (i.e., $\langle\ \rangle_\nu$ means averaging over the parameters of the νth interval, everything else being fixed). Then we have

$$\begin{aligned}\|\langle T(t,0)\rangle\| &= \|\langle T(t,nt_L)T_n\langle T_{n-1}T_{n-2}T_{n-3}\rangle_{n-2}T_{n-4}\\ &\qquad\times T_{n-5}\langle\cdots\rangle_{n-7}T_{n-9}\cdots T_5\langle T_4T_3T_2\rangle_3T_1\rangle\|\\ &\leqslant \Big\langle \prod_{\nu=1}^{n/5}\|\langle T_{5\nu-1}T_{5\nu-2}T_{5\nu-3}\rangle_{5\nu-2}\|\Big\rangle\\ &= \langle\|\langle T_4T_3T_2\rangle_3\|\rangle^{n/5}\end{aligned} \tag{2.2}$$

by stationarity and independence. This will yield the exponential falloff if the last expectation is less than 1. Assume that it is 1. This holds iff $\|\langle T_4T_3T_2\rangle_3\|$ is 1 with probability 1 or, equivalently, iff $\langle T_4T_3T_2\rangle_3$ has an eigenvalue of modulus 1 with probability 1.

By unitarity of the operators, averaging over any smaller set of parameters must also yield an eigenvalue of modulus 1. Now consider the event A that in $[0,2t_L]$ and $[3t_L,5t_L]$ there is no collision; this has nonzero probability. Let $A_0^{(3)}$ and $A_1^{(3)}$, $A_{0,1}^{(3)} \subset A$, be the events which are characterized by the additional condition that in $[2t_L,3t_L]$ there is no collision and one collision, respectively. For configurations in $A_0^{(3)}$ and $A_1^{(3)}$, $T_4T_3T_2$ equals $\mathbb{1}$ and the one-perturber S matrix, respectively. The latter, when averaged over $A_1^{(3)}$, cannot have the eigenvalue 1 since it does not have this eigenvalue in a neighborhood of $(\boldsymbol{\rho}^{(0)},\mathbf{v}^{(0)})$, by assumption and by continuity. Averaging $T_4T_3T_2$ over $A_0^{(3)} \cup A_1^{(3)}$, all resulting eigenvalues lie strictly *inside* the unit circle. Thus, for configurations in A, $\|\langle T_4T_3T_2\rangle_3\|$ is less than 1, proving exponential falloff in the case of zero ion potential.

For nonzero ion potential V_i, the same proof goes through verbatim, except that, on $A_0^{(3)}$ and $A_1^{(3)}$, $T_4T_3T_2$ equals $\exp(-iV_i 3t_L)$ and

$$
\begin{aligned}
&U(4t_L, t_L; V_i + \varphi(\boldsymbol{\rho}, \mathbf{v}; \cdot - \tau)) \\
&\quad = \exp\left[-iV_i(4t_L + \tau)\right] U(\infty, -\infty; \exp(iV_i \cdot)\varphi(\boldsymbol{\rho}, \mathbf{v}; \cdot)\exp(-iV_i \cdot)) \\
&\qquad \times \exp\left[iV_i(t_L + \tau)\right] \qquad (2.3)
\end{aligned}
$$

respectively; here $\tau \in [2t_L, 3t_L]$ denotes the collision time of the single electron. Averaging over $A_0^{(3)} \cup A_1^{(3)}$ and taking norms, the V_i-dependent terms can be dropped, and the reasoning is now as before. The case $t < 0$ is analogous. ■

We now consider the general case, i.e., the usual Maxwell velocity distribution.

Theorem 2.1. Consider a fixed ion potential. If, for some $\boldsymbol{\rho}^{(0)}$ and $\mathbf{v}^{(0)}$, the one-particle (electron) S matrix in the ion interaction picture does not have an eigenvalue 1, then $\|\langle T(t,0)\rangle\|$ falls off at least as $|t|^{-3+\epsilon}$ as $|t| \to \infty$ for any $\epsilon > 0$.

Proof. Let $t \gg 2\rho_D/v_0 \equiv t_0$ and let $t_L \equiv t_L(t) = t^{1-\epsilon/4}$. We denote by A_L the set of configurations for which all particles that are in the Debye sphere at some time between 0 and t spend less than time t_L therein. By Lemma A.3 the probability of the complement is bounded by const $\cdot$ t/t_L^4 + const$/t_L^3$. Hence

$$\|\langle T(t,0)\rangle\| \leqslant \|\langle \chi_{A_L} T(t,0)\rangle\| + \text{const}/t^{3-\epsilon} \qquad (2.4)$$

Again we consider the time intervals $[-t_L, 0], [0, t_L], \ldots$ of length t_L plus a remainder $[nt_L, t]$ with $0 \leqslant t - nt_L < 5t_L$ and n a multiple of 5. We decompose $T(t,0)$ as in Eq. (2.1). Since the set A_L arises from a velocity cutoff, χ_{A_L} factorizes into a product

$$\chi_{A_L} = \chi^{(1)} \cdots \chi^{(n+1)} \qquad (2.5)$$

where $\chi^{(\nu)}$ depends only on particles colliding in the νth interval. Then stationarity and independence yield, as in Eq. (2.2),

$$\|\langle \chi_{A_L} T(t,0)\rangle\| \leqslant \langle \|\langle \chi^{(3)} T_4 T_3 T_2\rangle_3\|\rangle^{n/5} \qquad (2.6)$$

where $n \sim t^{\epsilon/4}$. We complete the proof by showing that $\langle \cdots \rangle$ on the right-hand side is smaller than 1, uniformly in t_L. Since $T_4T_3T_2 = T(4t_L, t_L)$ depends on t through t_L, the previous proof has to be refined. We consider three consecutive time intervals of length $t_0 = 2\rho_D/\mathbf{v}^{(0)}$ starting at $2t_L$. Let A_0 be the set of configurations in A_L with no perturber in the sphere in all three time intervals, and let A_1 be the set with one perturber which collides in $[2t_L + t_0, 2t_L + 2t_0]$ with $(\boldsymbol{\rho}, \mathbf{v})$ values in a small neighborhood of $(\boldsymbol{\rho}^{(0)},$

$\mathbf{v}^{(0)}$) and with no other perturber entering or leaving in $[t_L, t_L + 3t_0]$. The single perturber under consideration thus has a complete collision in this interval. Furthermore, A_0 and A_1 have nonzero probability and, similarly to Eq. (2.3)

$$\chi_{A_0} T(4t_L, t_L) = \chi_{A_0} T(4t_L, 2t_L + 3t_0) \exp(-iV_i 3t_0) T(2t_L, t_L) \tag{2.7}$$

$$\begin{aligned}\chi_{A_1} T(4t_L, t_L) = \chi_{A_1} & T(4t_L, 2t_L + 3t_0) \\ & \times \exp\left[-iV_i(2t_L + 3t_0 + \tau)\right] \\ & \times S_I(\boldsymbol{\rho}, \mathbf{v}) \exp\left[iV_i(2t_L + \tau)\right] T(2t_L, t_L)\end{aligned} \tag{2.8}$$

where S_I is the one-particle S matrix in the ion interaction picture. Again $\chi_{A_{0,1}}$ factorize into

$$\chi_{A_{0,1}} = \chi_{A_{0,1}^{t_0}} \chi'_{A_{0,1}}, \qquad \chi^{(3)} = \chi_{3,t_0} \chi'_3 \tag{2.9}$$

where $\chi_{A_{0,1}^{t_0}}$ depends only on the variables of the interval $I_0 = [t_L, t_L + 3t_0]$ and $\chi'_{A_{0,1}}$ on the complement; correspondingly for $\chi^{(3)}$. We now denote by $\langle\ \rangle_{I_0}$ the average over the variables of the interval I_0. With Eqs. (2.7) and (2.8) we then obtain

$$\begin{aligned}\langle \| \langle \chi^{(3)} T_4 T_3 T_2 \rangle_3 \| \rangle & \leqslant \langle \| \langle \chi^{(3)} (\chi_{A_0} + \chi_{A_1}) T_4 T_3 T_2 \rangle_3 \| \rangle + \langle \chi^{(3)} (1 - \chi_{A_0} - \chi_{A_1}) \rangle \\ & \leqslant \langle \chi'_3 (\chi'_{A_0} + \chi'_{A_1}) \| \langle \chi_{3,t_0} (\chi_{A_0^{t_0}} \mathbb{1} + \chi_{A_1^{t_0}} S_I) \rangle_{I_0} \| \rangle \\ & \quad + \langle \chi^{(3)} (1 - \chi_{A_0} - \chi_{A_1}) \rangle\end{aligned} \tag{2.10}$$

Now we argue as in the preceding proof. The eigenvalues of $S_I(\boldsymbol{\rho}, \mathbf{v})$ have modulus 1, but none equals 1 in a neighborhood of $(\boldsymbol{\rho}^{(0)}, \mathbf{v}^{(0)})$. Since $A_0^{t_0}$ and $A_1^{t_0}$ are disjoint, one has

$$\| \langle \chi_{3,t_0} (\chi_{A_0^{t_0}} \mathbb{1} + \chi_{A_1^{t_0}} S_I) \rangle_{I_0} \| \leqslant \alpha \langle \chi_{3,t_0} (\chi_{A_0^{t_0}} + \chi_{A_1^{t_0}}) \rangle_{I_0} \tag{2.11}$$

with $\alpha < 1$ and α depending only on t_0. Eqs. (2.9) and (2.10) then yield

$$\langle \| \langle \chi^{(3)} T_4 T_3 T_2 \rangle_3 \| \rangle \leqslant \alpha < 1$$

independent of t (and t_L). The case $t < 0$ is proved similarly. ■

Remarks. (1) In the preceding results the ions are treated quasi-statically. For *moving ions* the results carry nearly literally over. The only change is that the previous one-perturber electron S matrix in the ion interaction picture is replaced by the one-particle electron *or* ion S matrix in the Schrödinger picture. This is easily seen by repeating the above proofs with two particle species and zero external field.

(2) We suspect that not only a power law decay but an exponential decay holds. This is true for instance for the (static) Holtsmark distribution. It can also be proved in the nonstatic case if the one-particle potentials commute and if the one-particle S matrix satisfies a condition similar to the

one above. In the commuting case $\langle T(t,0)\rangle$ can be expressed in closed form by the one-particle time-development operator.

(3) In concrete applications one has to check the conditions of Theorem 2.1 directly. The explicit form of the time-development operator given by Pfennig[13] for the case that the full Coulomb potential is replaced by the dipole term may be helpful.

(4) The methods of this section make use of the screening by a cutoff at the Debye sphere. It is possible that screening by means of a Debye–Hückel potential might be treated with a modification of our methods, e.g., by estimating the contribution from the exponential tails. It would be interesting to carry the results over to this more general case and to see whether the falloff is really not faster than t^{-3}. It would also be interesting to modify the criterion of Theorem 2.1 so as to involve the potential directly, not via the S matrix.

3. THE INTENSITY OPERATOR AS AN N-PERTURBER LIMIT

It is easy to see that the intensity operator $J_i(\omega)$ of Eq. (1.20) can be written as the time limit of a square, thus exhibiting its positivity properties explicitly (cf. Lemma 3.1). By probabilistic techniques it is then shown from this that the time limit can be replaced by a limit over collision times, which are random variables (Proposition 3.1). This in turn is used to replace the time limit by a limit over an increasing perturber number (Theorem 3.1). It is shown that the intensity operator is connected to tail events.

These results generalize results of Refs. 3 and 4. In Ref. 3 a lower velocity cutoff in the Maxwell velocity distribution was needed and the convergence was only in the sense of distributions; in Ref. 4 the velocity cutoff was removed. Here we obtain, without velocity cutoff, convergence in the stronger sense of convergence of measures and, more importantly, uniform convergence in ω if $\langle T(t,0)\rangle \in L^1$. These results will be basic for Part II.

Lemma 3.1. Let $\langle T(t,0)\rangle$ be absolutely integrable, i.e., in L^1. Then uniformly in ω

$$J_i(\omega) = \lim_{A\to\infty} (2\pi A)^{-1}\left\langle \left\{ \int_0^A dt\, e^{i\omega t} T(t,0)\right\} \{\cdots\}^* \right\rangle \tag{3.1}$$

If $\langle T(t,0)\rangle \notin L^1$, Eq. (3.1) still holds in the sense of weak convergence of measures.

Proof. For finite A, one can interchange expectation and integrations. By stationarity one has

$$\langle T(t,0)T(t',0)^*\rangle = \langle T(t-t',0)\rangle$$

By a change of variable one can then perform one integration, resulting in

$$(2\pi)^{-1}\int_{-A}^{A} dt\,(A-|t|)A^{-1}e^{i\omega t}\langle T(t,0)\rangle \tag{3.2}$$

If $\langle T(t,0)\rangle \in L^1$ this converges uniformly in ω to the Fourier transform of $T(t,0)$ as $A\to\infty$, by Lebesgue's bounded convergence.

If $\langle T(t,0)\rangle \notin L^1$, the Fourier transform of the right-hand side of Eq. (3.1) for finite A becomes a convolution. By stationarity this converges to $\langle T(t,0)\rangle$ as $A\to\infty$. By Levy's continuity theorem on convergence of positive measures and of characteristic functions[14] the statement follows. ∎

We now put

$$A=\langle\tau_N\rangle=N/c$$

in Eq. (3.1) and let $N\to\infty$, where c is the mean collision frequency. With some effort we will now prove the crucial result that the upper integration limit $A=\langle\tau_N\rangle$ in Eq. (3.1) can be replaced by the *random variable* τ_N. The difficulty in the proof is that stationarity cannot be used in the simple way as in Lemma 3.1 because the integration limit is a random variable.

Proposition 3.1. Let $\langle T(t,0)\rangle$ be in L^1. Then uniformly in ω

$$J_i(\omega)=\lim_{N\to\infty}(2\pi N)^{-1}c\left\langle\left\{\int_0^{\tau_N} dt\,e^{i\omega t}T(t,0)\right\}\{\cdots\}^*\right\rangle \tag{3.3}$$

If $\langle T(t,0)\rangle \notin L^1$, Eq. (3.3) still holds in the sense of weak convergence of measures.

Proof. Without loss of generality we can assume $c=1$. We first remark that the right-hand side of Eq. (3.4), without the limit, remains bounded in norm as $N\to\infty$. This follows from Eq. (A.5) by considering

$$\int_0^{\tau_N}-\int_0^{N}=\int_N^{\tau_N}$$

together with the crude estimate

$$N^{-1}\left\|\left\langle\left\{\int_N^{\tau_N} dt\,e^{i\omega t}T(t,0)\right\}\{\cdots\}^*\right\rangle\right\|\leqslant N^{-1}\langle(\tau_N-N)^2\rangle=1 \tag{3.4}$$

By this boundedness and by the inequality Eq. (A.6) we can replace the upper integration limit τ_N in Eq. (3.3) by τ_N+s_N, where s_N is positive, nonrandom and

$$s_N=o(N^{1/2}) \tag{3.5}$$

without changing a possible limit.

Now let $1/2<\alpha<1$. In Eq. (3.1) we take as upper integration limit $N+N^\alpha$. Since $N^\alpha/N\to 0$ we can then replace the factor $(N+N^\alpha)^{-1}$ by

N^{-1}. We now show that the difference of the resulting expression and of the right-hand side of Eq. (3.3) (without the "lim" and with upper integration $\tau_N + s_N$ instead of s_N) goes to 0 as $N \to \infty$. For this it suffices by the inequality (A.6) and the foregoing remark on boundedness that

$$N^{-1}\left\langle \left\{ \int_{\tau_N + s_N}^{N+N^\alpha} dt\, e^{i\omega t} T(t,0) \right\} \{ \cdots \}^* \right\rangle \to 0 \tag{3.6}$$

Let $\langle\ \rangle_{\tau_N = s}$ denote conditional expectation given that $\tau_N = s$ and let $p_{\tau_N}(\cdot)$ denote the density of the distribution function for τ_N. Then the expression in Eq. (3.6) can be written as a sum of three integrals,

$$N^{-1}\left\{ \int_0^{N-N^\alpha} + \int_{N-N^\alpha}^{N+N^\alpha - s_N} + \int_{N+N^\alpha - s_N}^{\infty} \right\} ds\, p_{\tau_N}(s)$$

$$\times \int_{S+s_N}^{N+N^\alpha} \int dt_1\, dt_2\, e^{i\omega(t_1 - t_2)} \langle T(t_1, t_2) \rangle_{\tau_N = s} \tag{3.7}$$

The third term can be estimated crudely as in Eq. (3.4) by

$$N^{-1} \int_{N+N^\alpha - s_N}^{\infty} ds\, p_{\tau_N}(s)(s + s_N - N - N^\alpha)^2$$

$$\leqslant P\{\tau_N \geqslant N + N^\alpha - s_N\}^{1/2} \langle \tau_N^4 \rangle^{1/2} N^{-1}$$

for N large.

By the variant of Bernstein's inequality in Lemma A.1 the first factor goes to zero faster than any power while $\langle \tau_N^4 \rangle = O(N^4)$. The first term is estimated similarly.

It remains to discuss the second term in Eq. (3.7). Since t_1 and t_2 are later than the Nth collision one may expect that $T(t_1, t_2)$ depends essentially only on the perturbers $N+1, N+2, \ldots$. Although their collision times are not independent of τ_N (only the intercollision times u_i are independent), this fact might somehow be exploited to replace $\langle\ \rangle_{\tau_N = s}$ by the ordinary expectation $\langle\ \rangle$.[5] Then one might be able to use stationarity and the fact that $\langle T(t,0) \rangle \in L^1$. In the following we make these heuristic remarks rigorous.

Lemma 3.2. If $\langle T(t,0) \rangle \in L^1$, then for $s_N = N^\beta$, with $0 < \beta < \frac{2}{3}\alpha - \frac{1}{3}$, the second term of Eq. (3.7) equals

$$N^{-1} \int_{N-N^\alpha}^{N+N^\alpha - s_N} ds\, p_{\tau_N}(s) \int_{s_N}^{N+N^\alpha - s} \int dt_1\, dt_2\, e^{i\omega(t_1 - t_2)} \langle T(t_1, t_2) \rangle + o(N)/N \tag{3.8}$$

[5] This was suggested to us by W. von Waldenfels.

Proof. Let B_N and B_N^0, respectively, be the sets of configurations for which those perturbers (electrons) which were in the Debye sphere at time τ_N and 0, respectively, are all outside the sphere at time $\tau_N + s_N$ and s_N, respectively. Let B_N^c and B_N^{0c} be the complements of these events. By Lemmas A.2 and A.4

$$\begin{aligned} P(B_N^{0c}) &= O(s_N^{-3}) \\ P(B_N^c) &= O(s_N^{-3}) \end{aligned} \tag{3.9}$$

Now we insert

$$\chi_{B_N} + \chi_{B_N^c} = 1$$

under the conditional expectation in the second term of Eq. (3.7) and write the whole expression as a sum of the two corresponding terms. The term with B_N^c can be estimated crudely by

$$N^{-1}\langle \chi_{B_N^c}(2N^\alpha - s_N)^2\rangle = O(N^{2\alpha - 3\beta})/N \tag{3.10}$$

which vanishes for $N \to \infty$.

For configurations in B_N and for $t_1, t_2 \geqslant \tau_N + s_N$ one has, suppressing velocities and impact parameters,

$$\begin{aligned} T(t_1, t_2) &= U\Big(t_1, t_2; V_i + \sum_{\nu > N} \varphi(\cdot - \tau_N - u_{N+1} - \cdots - u_\nu)\Big) \\ &= U\Big(t_1 - \tau_N, t_2 - \tau_N; V_i + \sum_{\nu > N} \varphi(\cdot - u_{N+1} - \cdots - u_\nu)\Big) \end{aligned} \tag{3.11}$$

since perturbers with collision time less than τ_{N+1} have already left the Debye sphere and thus do not contribute to the potential. Hence, by a change of the integration variables t_1 and t_2 to $t_1 - s$ and $t_2 - s$ one gets with Eq. (3.11)

$$\begin{aligned} &\iint_{s+s_N}^{N+N^\alpha} dt_1\, dt_2\, e^{i\omega(t_1 - t_2)} \langle \chi_{B_N} T(t_1, t_2)\rangle_{\tau_N = s} \\ &\quad = \iint_{s_N}^{N+N^\alpha - s} dt_1\, dt_2\, e^{i\omega(t_1 - t_2)} \\ &\qquad \times \Big\langle \chi_{B_N} U\Big(t_1, t_2; V_i + \sum_{\nu > N} \varphi(\cdot - u_{N+1} - \cdots - u_\nu)\Big)\Big\rangle_{\tau_N = s} \end{aligned} \tag{3.12}$$

By Eqs. (3.9) and (3.10), χ_{B_N} can again be replaced by 1, with error $o(N)$. But the remaining random variable under the conditional expectation is independent of τ_N, and thus $\langle \cdots \rangle_{\tau_N = s} = \langle \cdots \rangle$. Furthermore, since the intercollision times u_i are independent and identically distributed, one can replace $\sum_{\nu>N}$ by $\sum_{\nu>0}$.

By Eq. (3.9) one can now insert $\chi_{B_N^0}$ under the expectation, with error $o(N)$. But for a configuration in B_N^0 one has, if $t_1, t_2 \geqslant s_N$,

$$T(t_1, t_2) = U\Big(t_1, t_2; V_i + \sum_{\nu>0} \varphi(\cdot - u_1 - \cdots - u_\nu)\Big)$$

[cf. Eq. (3.11)]. After inserting this into Eq. (3.12) (with $B_N \to B_N^0$, $\sum_{\nu>N} \to \sum_{\nu>0}$) one can again omit $\chi_{B_N^0}$ with error $o(N)$, and thus arrive at Eq. (3.8). ■

Proof of Proposition 3.1 (continued). Stationarity and a change of variable in Eq. (3.8) yields the estimate

$$N^{-1}\int_{N-N^\alpha}^{N+N^\alpha - s_N} ds\, p_{\tau_N}(s)(N + N^\alpha - s - s_N)\int_{-\infty}^{\infty} dt\, \|\langle T(t,0)\rangle\|$$
$$\leqslant N^{-1}(2N^\alpha - N^\beta)\cdot \text{const}$$

which converges to 0 as $N \to \infty$. This proves the first part of the proposition.

If $T(t,0) \notin L^1$, one can consider Fourier transforms and convolutions as in Ref. 4 and then proceed as in the proof of the second part of Lemma 3.1. ■

Corollary 3.1. In Eq. (3.3) one can replace $T(t,0)$ by

$$U\Big(t, 0; V_i + \sum_{\nu=1}^{N} \varphi(\cdot - \tau_\nu + \tau_1)\Big) \tag{3.13}$$

the time-development operator for the ions and the first N electrons colliding after $t = 0$, shifted by τ_1, so that the first collision is at $t = 0$.

Proof. In Eq. (3.3) the lower and upper integration limits can be replaced by $N^\beta + \tau_1$ and $\tau_N - N^\beta + \tau_1$, respectively, $0 < \beta < 1/2$, by Corollary A.1. By Bernstein's inequality (Lemma A.1), one can assume

$$(N - N^\alpha)c^{-1} \leqslant \tau_N \leqslant (N + N^\alpha)c^{-1}$$

with $1/2 < \alpha < 1$. Similarly as in Eqs. (3.9)–(3.11) one then concludes the statement by Lemmas A.2 and A.4. ■

We are now in a position to derive two expressions for the intensity operator in which the time limit is replaced by a limit over increasing perturber numbers. These still exact expressions will be the starting point for subsequent approximations. It is convenient to go into the interaction picture.

Theorem 3.1. Let the time-shifted N-electron potential in the ion interaction picture be defined by[6]

$$\phi(1\ldots N;t):=\exp(iV_it)\sum_{\nu=1}^{N}\varphi(t-\tau_\nu+\tau_1)\exp(-iV_it) \tag{3.14}$$

With this potential let the random operator $\mathscr{D}(1\ldots N;\omega)$ and $\mathscr{T}(1\ldots N;\omega)$ be defined by[7]

$$\mathscr{D}(1\ldots N;\omega):=\int dt\, e^{i(\omega-V_i)t}\phi(1\ldots N;t)U(t,-\infty;\phi(1\ldots N)) \tag{3.15}$$

$$\begin{aligned}\mathscr{T}(1\ldots N;\omega):=\int dt\, e^{i(\omega-V_i)t}\,\{&U(t,-\infty;\phi(1\ldots N))-g(t)\mathbb{1}\\ &-(1-g(t-u_1-\cdots-u_N))U(\infty,-\infty;\phi(1\ldots N))\}\end{aligned} \tag{3.16}$$

where the real function g satisfies

$$\int_0^\infty |g(t)|\,dt<\infty,\qquad \int_{-\infty}^0 |1-g(t)|\,dt<\infty \tag{3.17}$$

Then, if $\langle T(t,0)\rangle\in L^1$, one has *uniformly* in ω

$$J_i(\omega)=\lim_{N\to\infty}(2\pi N)^{-1}c\langle\mathscr{T}(1\ldots N;\omega)\mathscr{T}(1\ldots N;\omega)^*\rangle \tag{3.18}$$

and

$$(\omega-V_i)J_i(\omega)(\omega-V_i)=\lim_{N\to\infty}(2\pi N)^{-1}c\langle\mathscr{D}(1\ldots N;\omega)\mathscr{D}(1\ldots N;\omega)^*\rangle \tag{3.19}$$

If $\langle T(t,0)\rangle\notin L^1$, the convergence is in the sense of weak convergence of measures.

Proof. Note that $\mathscr{D}$ and $\mathscr{T}$ are well defined. Indeed, the integrand in Eq. (3.15) has compact support with probability 1, and so has that in Eq. (3.16) if one chooses

$$g(t)=\chi_{(-\infty,0]}(t)\equiv\theta(-t)$$

For general g one then uses Eq. (3.17).

The expression in Eq. (3.13) equals

$$\exp(-iV_it)U(t,0;\phi(1\ldots N)) \tag{3.20}$$

[6] The time shift is such as to have the first collision at $t=0$.

[7] The expression in the curly bracket in Eq. (3.16) is essentially the time-development operator for $\phi(1\ldots N,t)$ with additional terms to get compact support or at least integrability. The time shift in g has been chosen in view of algebraic relations to be derived in Part II.

by which we replace $T(t,0)$ in Eq. (3.3). Upon insertion into Eq. (3.3) the initial time $t'=0$ can be replaced by $-\infty$ since the additional terms cancel each other. The curly bracket in Eq. (3.3) can then be written as

$$\left\{\int_0^{\tau_N} dt\, e^{i(\omega-V_i)t}\left[U(t,-\infty;\phi(1\ldots N))-\theta(-t)\right.\right.$$
$$\left.\left.-\theta(t-\tau_N)U(\infty,-\infty;\phi(1\ldots N))\right]\right\} \tag{3.21}$$

since for $t\in(0,\tau_N)$ the additional terms are zero.

We now show that the integration limits can be taken to $-\infty$ and $+\infty$. Using the Schwarz-type inequality of Theorem A.1 we first consider

$$N^{-1/2}\left\langle\left\{\int_{\tau_N}^{\infty} dt\,\| U(t,-\infty;\phi(1\ldots N))-\theta(-t)\right.\right.$$
$$\left.\left.-\theta(t-\tau_N)U(\infty,-\infty;\phi(1\ldots N))\|\right\}^2\right\rangle^{1/2}$$
$$\leqslant N^{-1/2}\sum_{\mathrm{m}\geqslant 0}\left\langle\left\{\int_{\tau_N+\mathrm{m}}^{\tau_N+\mathrm{m}+1} dt\,\|\cdots\|\right\}^2\right\rangle^{1/2} \tag{3.22}$$

where the triangle inequality has been used. The mth integrand vanishes unless at least one of the first N perturbers is still in the Debye sphere at time $\tau_N+\mathrm{m}$, which has probability $O(\mathrm{m}^{-3})$, by Lemma A.4. Hence we get for Eq. (3.22) the estimate

$$\leqslant N^{-1/2}\mathrm{const}\left(1+\sum_{\mathrm{m}\geqslant 1}\mathrm{m}^{-3/2}\right)$$

which goes to zero for $N\to\infty$. The integral from $-\infty$ to 0 is treated similarly.

The introduction of the function g is now straightforward by means of Eq. (3.17). This then yields Eq. (3.18).

Equation (3.19) is now derived by a simple partial integration. From Eq. (3.16) one has

$$\mathscr{D}(1\ldots N;\omega)=\lim_{\kappa\to\infty} i\int_{-\kappa}^{\kappa} dt\, e^{i(\omega-V_i)t}\frac{d}{dt}U(t,-\infty;\phi(1\ldots N))$$
$$=\lim_{\kappa\to\infty} i\left[e^{i(\omega-V_i)\kappa}U(\infty,-\infty;\phi(1\ldots N))-e^{-i(\omega-V_i)\kappa}\right.$$
$$\left.-i(\omega-V_i)\int_{-\kappa}^{\kappa} dt\, e^{i(\omega-V_i)t}U(t,-\infty;\phi(1\ldots N))\right] \tag{3.23}$$

With

$$e^{\pm i(\omega - V_i)\kappa} = i(\omega - V_i)\int_0^{\pm\kappa} dt\, e^{i(\omega - V_i)t} + \mathbb{1}$$

we can write Eq. (3.23) as

$$\begin{aligned}\mathscr{D}(1 \ldots N; \omega) = i\big[\, U(\infty, -\infty; \phi(1 \ldots N)) - \mathbb{1}\,\big] \\ + (\omega - V_i)\int dt\, e^{i(\omega - V_i)t}\, \{ U(t, -\infty; \phi(1 \ldots N)) - \theta(-t) \\ - \theta(t)\, U(\infty, -\infty; \phi(1 \ldots N))\}\end{aligned} \tag{3.24}$$

Furthermore we have

$$\begin{aligned} i(\omega - V_i)\int dt\, e^{i(\omega - V_i)t}\big[\,\theta(t) - \theta(t - u_1 - \cdots - u_N)\big] \\ = \int_0^{u_1 + \cdots + u_N} dt \frac{d}{dt} e^{i(\omega - V_i)t} = e^{i(\omega - V_i)\sum_1^N u_\nu} - \mathbb{1} \end{aligned} \tag{3.25}$$

Now Eq. (3.19) follows from the Schwarz-type inequality in Theorem A.1 since the bounded terms vanish after division by N when $N \to \infty$.

The last statement of the theorem can be proved along similar lines by Fourier transforming and using convolutions. ■

Connection with Tail Events. The time origin $t = 0$ plays no distinguished role in the preceding. By now familiar techniques the lower integration limit $t = 0$ in Eqs. (3.1) and (3.3) can be replaced by $t = \tau_M$ for any fixed M. In Theorem 3.1 the perturbers $1, \ldots, N$ are then replaced by the perturbers $M, \ldots, N$ with $N \to \infty$. Since the result is independent of M, one can let M grow arbitrarily. This shows that only the "tail" of the perturbers for arbitrarily large collision time determine the intensity operator.

Several Perturber Species. All results of this section carry directly over to several perturber species. This is due to the fact that the sum of two Poisson processes is again a Poisson process. The κth collision can be by any of the perturber species and one just has an additional parameter over which to average. The collision frequencies just add.

In Part II we will insert a noncommutative cluster expansion into Eqs. (3.18) and (3.19). The limit over the perturber numbers, $N \to \infty$, can then be performed explicitly. This leads to an expansion of the intensity operator in terms of truncated quantities from which correlations have been removed.

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APPENDIX: INEQUALITIES AND ESTIMATES

If A is a random operator in a Hilbert space, we define its expectation $\langle A\rangle$ by

$$(\varphi, \langle A\rangle\psi) := \langle(\varphi, A\psi)\rangle \tag{A.1}$$

if the right-hand side exists. Here we consider only the case where one obtains bounded operators. A sufficient condition for this is that

$$\langle\|A\|\rangle < \infty$$

due to the inequality

$$\|\langle A\rangle\| \leqslant \langle\|A\|\rangle \tag{A.2}$$

The following theorem, whose proof will appear elsewhere, is a Schwarz-type inequality for random operators.

Theorem A.1.[15] Let A, B be random (bounded) operators in a Hilbert space. Then

$$\|\langle A^*B\rangle\|^2 \leqslant \|\langle A^*A\rangle\|\|\langle B^*B\rangle\| \tag{A.3}$$

From this one obtains a triangle-type inequality and other useful inequalities.

Corollary A.1.

$$\|\langle(A+B)^*(A+B)\rangle\|^{1/2} \leqslant \|\langle A^*A\rangle\|^{1/2} + \|\langle B^*B\rangle\|^{1/2} \tag{A.4}$$

$$\big|\|\langle A^*A\rangle\|^{1/2} - \|\langle B^*B\rangle\|^{1/2}\big| \leqslant \|\langle(A-B)^*(A-B)\rangle\|^{1/2} \tag{A.5}$$

$$\begin{aligned}\|\langle A^*A\rangle - \langle B^*B\rangle\| \leqslant{}& \{\|\langle A^*A\rangle\|^{1/2} + \|\langle B^*B\rangle\|^{1/2}\}\\ &\times \|\langle(A-B)^*(A-B)\rangle\|^{1/2}\end{aligned} \tag{A.6}$$

The next result is a variant of the well-known Bernstein inequality[16] whose proof is based on Chebyshev's inequality

$$P\{|X| \geqslant a\} \leqslant a^{-1}E|X| \tag{A.7}$$

Lemma A.1. Let $u_1, \ldots, u_n$ be independent identically distributed random variables with common density $c\exp(-cx)$ for $x > 0$ and zero otherwise. Then

$$P\left\{u_1 + \cdots + u_n > (n + kn^{1/2})c^{-1}\right\} \leqslant \exp(-k^2/4) \tag{A.8}$$

$$P\left\{u_1 + \cdots + u_n < (n - kn^{1/2})c^{-1}\right\} \leqslant \exp(-k^2/4) \tag{A.9}$$

for $0 \leqslant k \leqslant n^{1/2}$.

Proof. The assumptions of the general result in Ref. 15 are not fulfilled, but the proof can be modified in a simple way as follows. Let

$$\gamma = \tfrac{1}{2}kcn^{-1/2}$$

Then $0 \leqslant \gamma/c \leqslant 1/2$ and

$$E\exp\{\gamma(u_1 + \cdots + u_n)\} = (1 - \gamma/c)^{-n}$$

In the Chebyshev inequality (A.7) we now choose

$$X = \exp[\gamma(u_1 + \cdots + u_n)]/E\exp[\gamma(u_1 + \cdots + u_n)]$$

$$a = \exp(k^2/4)$$

Note that $E|X| = 1$. Now one has from the series for $\ln(1 - x)$ that

$$-x^{-1}\ln(1 - x) \leqslant 1 + \tfrac{1}{2}x(1 - x)^{-1} \leqslant 1 + x$$

for $0 < x \leqslant 1/2$. Hence

$$\begin{aligned}\{X \geqslant a\} &= \left\{u_1 + \cdots + u_n \geqslant -n\gamma^{-1}\ln(1 - \gamma/c) + k^2/4\gamma\right\}\\ &\supset \left\{u_1 + \cdots + u_n \geqslant n/c + \gamma n/c^2 + k^2/4\gamma\right\}\end{aligned}$$

Inserting for γ then yields Eq. (A.8). Replacing γ by $-\gamma$ one obtains Eq. (A.9) in a similar way. ■

The probability P_n of finding n perturbers inside the sphere with radius ρ_D and volume V_D at a given time is

$$P_n = \frac{(\nu V_D)^n}{n!}e^{-\nu V_D} \tag{A.10}$$

where ν is the (mean) density. The probability $P_m(s)$ that exactly m particles enter (or, respectively, leave) the sphere in a time interval of length s is

$$P_m(s) = \frac{(cs)^m}{m!}e^{-cs} \tag{A.11}$$

where c is the (mean) collision frequency. This is well known and seen by elementary arguments.

Lemma A.2. Consider the particles inside the Debye sphere at some time t_0. The probability that at least one of them is inside the sphere at time $t_0 + t$ behaves as $O(t^{-3})$ for large $|t|$.

Proof. Without loss of generality we take $t_0 = 0$. An upper bound for the time the κth particle spends in the Debye sphere is given by

$$\sigma = 2\rho_D / v_k$$

The Maxwell distribution yields a density function for σ proportional to

$$\sigma^{-4}\exp(-\text{const}\,\sigma^{-2}) \tag{A.12}$$

This immediately implies

$$P\{\sigma > |t|\} \leqslant \text{const}\,|t|^{-3}$$

The probability to find, from n particles in the Debye sphere at time 0, at least one still inside at time t is then bounded by

$$1 - (1 - P\{\sigma > |t|\})^n \leqslant nP\{\sigma > |t|\} \tag{A.13}$$

Multiplying this by P_n from Eq. (A.10) and summing over n we get the desired result.

Lemma A.3. Consider the set of those particles each of which is in the Debye sphere at some time in $[0, t]$. The probability that at least one of them has a collision duration longer than t_L, for some t_L, is bounded by

$$1 - \exp(-\text{const}\,t/t_L^4) + O(t_L^{-3}) \tag{A.14}$$

Proof. First we consider the particles with collision time in $[0, t]$. The probability that there are n of these is, by the Poisson distribution,

$$\frac{(c|t|)^n}{n!}e^{-c|t|} \tag{A.15}$$

The velocity distribution Eq. (1.15) contains an additional factor v. This now changes in Eq. (A.11) σ^{-4} into σ^{-5}. Hence, for a single particle colliding in $[0, t]$,

$$P\{\sigma \geqslant t_L\} \leqslant \text{const}\,t_L^{-4}$$

Multiplying by Eq. (A.15) and summing over n we obtain

$$1 - \exp(-\text{const}\,t/t_L^4) \tag{A.16}$$

which is the first term in Eq. (A.14). Now we apply Lemma A.2 to the particles inside the sphere at time 0 and t, resulting in $O(t_L^{-3})$. The sum of the two probabilities gives an upper bound for the probability in question. ∎

Lemma A.4. Let τ_N be the collision time of the Nth perturber, which is a random variable, and consider the particles inside the Debye sphere at this time. Then the probability that at least one of them is inside the sphere at time $\tau_N + t$ behaves as $O(|t|^{-\frac{3}{2}})$ for large $|t|$, uniformly in N.

Proof. The probability of finding $(n + 1)$ particles in the sphere at time τ_N is the same as the conditional probability of finding n additional particles inside the sphere given that one particle is at its point of closest approach. By independence this probability is just P_n of Eq. (A.1). Now the argument proceeds as in the previous proof.

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