

Integral expansion often reducing to the density-gradient expansion, extended to non-Markov stochastic processes: Consequent non-Markovian stochastic equation whose leading terms coincide with Schrödinger's

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(Received 10 July 1989)

An integral expansion is obtained that reduces under explicitly given conditions to the density-gradient expansion for the number density of stochastic particles. Explicit coefficients in terms of moments are calculated up to and including the fourth order, corresponding to the super-Burnett approximation. The expansion is proven to be valid for both Markov and non-Markov processes, including those with infinite memory, typical of a stochastic motion with inertia. An application of this expansion is the relation between local average velocities in Markovian stochastic processes and the drift velocity of a probability cloud. As a further application we obtain a non-Markovian stochastic equation whose leading terms coincide with the Schrödinger equation. The additional terms could be interpreted as corrections that produce contributions to atomic spectra of the fine-structure type. In the case of scattering, where the density gradients can be locally high, the correction terms become relevant and they could perhaps explain the differences between the calculated and measured rotational and/or vibrational cross sections for hydrogen molecules.

I. INTRODUCTION

The density-gradient expansion is fundamental for drift and diffusion of free electrons in slightly ionized gases, and is extensively used in the treatises on this subject.¹

Expansions in terms of density gradients were already implicit in the works of Wannier² and Kihara.³ The first use of Fourier expansion in order to find density-gradient expansions was by Parker and Lowke.⁴ Both approaches have been discussed by Kumar and Robson⁵ and by Skullerud⁵ and extensive discussions and applications of the continuity equation are contained in the book of Huxley and Crompton.¹

An expansion in density gradients up to and including the third order (Burnett approximation) has been given by Tagashira *et al.*⁶ in the case of $\nabla\rho$ (where ρ is the normalized number density) parallel to the acceleration $\mathbf{a}=e\mathbf{E}/m$, where \mathbf{E} is the external electric field, e the charge, and m the mass. Because of this limitation (not explicitly emphasized in their work) this paper has been strongly criticized by Robson and Ness.⁷ Moreover, no use is made of the momenta \mathbf{M}_m independent of the velocity \mathbf{v} [see Eq. (3) later] because $f(\mathbf{k}, t)$ [Eq. (5) later] is not introduced and therefore the second expansion [Eq. (6) later] not carried out.

The density-gradient expansion is assumed as a starting point in the paper by Kumar, Skullerud, and Robson,⁸ which constitutes the most recent theoretical treatise on the kinetic theory of charged particle swarms in neutral gases. In a subsequent paper, Kumar⁸ starts in Eq. (1) with the postulated validity of the density-gradient expansion.

A slightly different procedure to obtain the first three terms (i.e., up to and including $\nabla\nabla$) of the gradient density expansion has been given by Penetrante and Bardsley.⁹

However, all the aforementioned authors have given a partial proof of the density-gradient expansion and have not clarified its limitations that appear from our Eqs. (5) and (6) never used by them. They start from the Fourier integral (which is a very general tool), expand the exponential as in our Eq. (4), and substitute the result in the Boltzmann equation which, to be solved, implies the knowledge of the distribution function $F(\mathbf{r}, \mathbf{V}t)$ of the scattering centers, in particular of the reference system in which F is isotropic. This limits the validity of the expansion to Markov processes, including the nonhydrodynamic regime. The memory implied in the latter, for instance for electrons moving through gas molecules that have not yet reached a thermalization, has nothing to do with the memory implied in a non-Markov process. In the latter, the stochastic environment that produces the jiggling motion of the electrons changes with time. On the contrary, in the Markovian nonhydrodynamic regime the stochastic environment (for instance the molecules) is stationary. Mathematically, the situation of electrons in gases is well characterized by a time-dependent conditional (or transition) probability density containing the situation at only one preceding time. For a non-Markov process two or more preceding situations are necessary.¹⁰ For a stochastic motion with inertia, as that of a rocket in vacuo emitting random bullets (or short period jets) with an average isotropic distribution, infinite preceding situations are necessary if external deterministic forces (as gravity) act on the rocket. The infinite memory implied in this process is completely different from the memory in the Markovian hydrodynamic regime. Indeed the gas molecules, in order to produce a stochastic motion as that of the considered rocket, should accelerate so as to have an isotropic distribution, with respect to the instantaneous rest observer of the electron distribution.

The differences between a non-Markov process and the nonhydrodynamic Markov process are still more evident if we consider the relevant power spectral densities (spectra), which characterize a stochastic process if it is Gaussian (as practically occurs for any physical system). The spectrum of the nonhydrodynamic Markov process is Lorentzian, i.e., “white” up to an upper cutoff frequency. For free electrons in neutral molecules (which constitute an example of Brownian motion), the power spectral density is frequency independent up to the average collision frequency of electrons with molecules. On the contrary, the spectrum of a non-Markov process is “colored”.

The most important non-Markov process is that of a stochastic motion with inertia. It is infinitely non-Markovian because all the preceding history of the external forces must be known. It can have either an external or an internal origin. The external origin is due to collisions with other particles or interactions with fields, typically the electromagnetic field. In this case there is only one stochastic process allowing a motion with inertia and it is characterized by a power spectral density proportional to ω^3 (where ω is the angular frequency). This spectrum, which is at the basis of stochastic electrodynamics, is the only one to be Lorentz invariant, and therefore to be the same for any inertial observer.¹¹ The internal origin of a stochastic motion with inertia is that of the considered rocket in vacuo emitting random bullets. In this case the spectrum of the emission is not important and the process can even be non-Gaussian and therefore not completely characterized by its power spectrum. This stochastic motion is that of quantum mechanics.¹²

Recently, Nadim, Pagitsas, and Brenner¹³ have developed a novel moment-gradient expansion for the phase-space distribution function relevant to neutral particles undergoing a Brownian motion, for which the effects due to external fields are irrelevant. They use our Eqs. (5) and (6) but do not discuss the limitations for the expansions. Moreover, which is the fundamental point, they do not even use the general Boltzmann equation but only “constitutive equations” so that they restrict their approach to Markov processes.

It seems therefore worthwhile to give clear and concise proof of the density-gradient expansion, at the same time showing what the maximum allowable gradients are and extending the validity of the expansion to non-Markov processes, for which there are no simulations as those (mainly obtained by the Monte Carlo method) relevant to Markov processes in either the hydrodynamical or nonhydrodynamical regime. Still better, in Sec. II, we give an expansion of integrals that is always valid (even for discontinuous functions) and that reduces, under explicitly given conditions, to the density-gradient expansion.

In Sec. III we give a novel application of the density-gradient expansion by finding the difference between the local average velocity and the drift velocity of a probability cloud, always for a generic, in general non-Markovian stochastic process.

In Sec. IV we apply the result of Sec. III to the sto-

chastic motion with inertia that produces the quantum effects. If we limit the density-gradient expansion to the first three terms the usual Schrödinger equation is obtained.¹² This fundamental equation for nonrelativistic quantum mechanics without spin is therefore no longer seen as axiomatic and immutable but only as a first-order approximation of a stochastic process. First order only because the first term of the density-gradient expansion is zero when there is particle number conservation as is the case for Schrödinger equation. The first nonzero term represents the zero-order approximation and gives the classical results. The successive, first-order term gives the quantum effects included in the Schrödinger equation. The inclusion of a second-order term as done in Sec. IV, leads to a generalized, or more refined, Schrödinger-like equation that should give the same results obtainable by the usual Schrödinger equation in the majority of the cases. Only in some few cases, where there is disagreement between experiments and theoretical results, obtainable by using the Schrödinger equation, it is hoped that the new generalized equation can give predictions in agreement with experiments.

II. DERIVATION OF THE INTEGRAL EXPANSION FOR A GENERAL STOCHASTIC PROCESS. ITS REDUCTION UNDER EXPLICITLY GIVEN CONDITIONS TO THE USUAL DENSITY-GRADIENT EXPANSION

Let us start, following Nadim *et al.*¹³ with the probability density $f(\mathbf{r}, \mathbf{v}, t)$ in the phase space (\mathbf{r} is the position, \mathbf{v} the velocity, and t the time), whose marginal distribution, upon integration over \mathbf{v} , is the probability density in the configuration space

$$\rho(\mathbf{r}, t) = \int d^3\mathbf{v} f(\mathbf{r}, \mathbf{v}, t). \quad (1)$$

Define the moments

$$\mathbf{P}_m(\mathbf{v}, t) = \int d^3\mathbf{r} \mathbf{r}^m f(\mathbf{r}, \mathbf{v}, t) \quad (2)$$

and

$$\mathbf{M}_m(t) = \int d^3\mathbf{v} \mathbf{v} \mathbf{P}_m(\mathbf{v}, t), \quad (3)$$

expand the exponential in the Fourier transform of f and use Eq. (2),

$$\begin{aligned} \tilde{f}(\mathbf{k}, \mathbf{v}, t) &= \int d^3\mathbf{r} f(\mathbf{r}, \mathbf{v}, t) \exp(i\mathbf{k} \cdot \mathbf{r}) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} (i\mathbf{k})^{\circ(n)} \mathbf{P}_n(\mathbf{v}, t), \end{aligned} \quad (4)$$

where n denotes n scalar multiplications in the order prescribed by the “nesting convention” of Chapman and Cowling.¹⁴

Integrating Eq. (4) over \mathbf{v} gives, with the use of Eq. (3) and the normalization to unity of f and ρ ,

$$\tilde{f}(\mathbf{k}, t) = \int d^3\mathbf{v} f(\mathbf{k}, \mathbf{v}, t) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} (i\mathbf{k})^{\circ(n)} \mathbf{M}_n(t). \quad (5)$$

Let us divide Eq. (4) by Eq. (5) and expand the second side by the binomial series

$$\frac{\tilde{f}(\mathbf{k}, \mathbf{v}, t)}{\tilde{f}(\mathbf{k}, t)} = \sum_{n=0}^{\infty} \frac{1}{n!} (i\mathbf{k})^{n\odot(n)} \mathbf{P}_n(\mathbf{v}, t) \left[1 + \sum_{j=1}^{\infty} (-1)^j \left[\sum_{s=1}^{\infty} \frac{1}{s!} (i\mathbf{k})^{s\odot(s)} \mathbf{M}_s \right]^j \right] = \sum_{n=0}^{\infty} (i\mathbf{k})^{n\odot(n)} \mathbf{Q}_n(\mathbf{v}, t), \quad (6)$$

where the tensors \mathbf{Q}_n are combinations of \mathbf{P}_n and \mathbf{M}_n . The expansion (6) is valid when the absolute value of the series in Eq. (5) is less than 1 and this is always possible provided the wave number k is less than a maximum value k_M satisfying

$$(\mathbf{k}_M \cdot \mathbf{M}_1)^2 + (\frac{1}{2} \mathbf{k}_M^2 \odot^2 \mathbf{M}_2)^2 = 1. \quad (7)$$

Indeed the series in (5) can be divided into two series, one real and the other imaginary, each of which with alternating signs and terms with decreasing values if Eq. (7) is satisfied. For instance, if $f(\mathbf{r}, \mathbf{v}, t)$ is given by an either bivariate or non-Gaussian distribution, centered in \mathbf{r}_0 with spread σ , Eq. (7) implies $k_M^{-1} = \lambda/2\pi \sim (r_0^2 + \sigma^2)^{1/2}$. The two next terms of the expansion are of the kind $k^4(r_0^2 + \sigma^2)^2 < 1$ and so on. Consequently, the convergence of the binomial expansion is better if we retain the whole series in Eq. (5). The convergence is then valid with any truncation provided $k < k_M$ with k_M given by (7).

Let us multiply Eq. (6) by $f(\mathbf{k}, t)$ and take a "limited" Fourier antitransform (with $k \leq k_M$), also using Eqs. (1), (4), and (5), the identity

$$i\mathbf{k} \exp(i\mathbf{k} \cdot \mathbf{r}) = \nabla \exp(i\mathbf{k} \cdot \mathbf{r})$$

and integrating by parts over \mathbf{r} with the condition ρ (boundary) = 0. We get

$$f(\mathbf{r}, \mathbf{v}, t) \simeq \sum_{n=0}^{\infty} \mathbf{Q}_n \odot^n \int d^3 \mathbf{r}' (-\nabla)^n \rho(\mathbf{r}') (2\pi)^{-3} \times \int_{-k_M}^{k_M} d^3 k \exp[i\mathbf{k} \cdot (\mathbf{r}' - \mathbf{r})]. \quad (8)$$

When k_M is sufficiently large the last integral in (8) is a rapidly oscillating function of \mathbf{r}' with a narrow bell-shaped envelope centered on \mathbf{r} (where it acquires a very high positive value) and tends to $\delta(\mathbf{r} - \mathbf{r}')$ for $k_M \rightarrow \infty$. Thus, if $\nabla \rho(\mathbf{r}')$ is rather regular and not very high for $\mathbf{r}' \neq \mathbf{r}$, Eq. (8) can be reduced with sufficient approximation to

$$f(\mathbf{r}, \mathbf{v}, t) \sim \sum_{n=0}^{\infty} \mathbf{Q}_n(\mathbf{v}, t) \odot^n (-\nabla)^n \rho(\mathbf{r}, t). \quad (9)$$

When the aforementioned conditions are not satisfied one has to use Eq. (8), as in the case of discontinuous functions. For example, consider the following discontinuous function, which may be an admissible initial condition

$$f(\mathbf{r}, \mathbf{v}) = \left[\frac{m}{2\pi kT} \right]^{3/2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] \times \left[1 + \frac{3\mathbf{v}\mathbf{v} - v^2 \mathbf{I}}{v^2 + c^2} : \tilde{\mathbf{e}} \mathbf{g}(\mathbf{r}) \right] \frac{3}{R^3} H(R - r), \quad (10)$$

where T is a constant temperature, c a constant speed, $\tilde{\mathbf{e}}$ a small constant dimensionless dyadic, $H(z)$ the step function ($H=1$ for $z \geq 0$ and $H=0$ for $z < 0$), R a constant radius, and $g(r)$ a general bounded function of position. $\tilde{\mathbf{e}}$ is chosen so small that f is non-negative. Clearly, when

$$r < R, \quad \rho(\mathbf{r}) = \int d^3 \mathbf{v} f(\mathbf{r}, \mathbf{v}) = 3/R^3$$

so that the right-hand side of Eq. (9) would be independent of \mathbf{r} , at variance with the \mathbf{r} dependence of its left-hand side. On the contrary, the integral expansion (8) reproduces rather well the given $f(\mathbf{r}, \mathbf{v})$ similarly to the Fourier transform of a discontinuous function.

The coefficients \mathbf{Q}_n are the same in both (8) and (9) and we give their explicit expressions up to $n=4$, corresponding to the super-Burnett approximation

$$\mathbf{Q}_0 = \mathbf{P}_0(\mathbf{v}, t), \quad (11)$$

$$\mathbf{Q}_1 = \mathbf{P}_1(\mathbf{v}, t) - P_0(\mathbf{v}, t) \mathbf{M}_1(t), \quad (12)$$

$$\mathbf{Q}_2 = \frac{1}{2} \mathbf{P}_2 - \mathbf{P}_1 \mathbf{M}_1 + P_0(\mathbf{M}_1^2 - \frac{1}{2} \mathbf{M}_2), \quad (13)$$

$$\mathbf{Q}_3 = \frac{1}{6} \mathbf{P}_3 - \frac{1}{2} \mathbf{P}_2 \mathbf{M}_1 + \mathbf{P}_1(\mathbf{M}_1^2 - \frac{1}{2} \mathbf{M}_2) - P_0(\mathbf{M}_1^3 - \mathbf{M}_1 \mathbf{M}_2 + \frac{1}{6} \mathbf{M}_3), \quad (14)$$

$$\mathbf{Q}_4 = \frac{1}{24} \mathbf{P}_4 - \frac{1}{6} \mathbf{P}_3 \mathbf{M}_1 + \frac{1}{2} \mathbf{P}_2(\mathbf{M}_1^2 - \frac{1}{2} \mathbf{M}_2) - \mathbf{P}_1(\mathbf{M}_1^3 - \mathbf{M}_1 \mathbf{M}_2 + \frac{1}{6} \mathbf{M}_3) + P_0(\mathbf{M}_1^4 - \frac{3}{2} \mathbf{M}_1^2 \mathbf{M}_2 + \frac{1}{3} \mathbf{M}_1 \mathbf{M}_3 + \frac{1}{4} \mathbf{M}_2^2 - \frac{1}{24} \mathbf{M}_4). \quad (15)$$

So far the procedure is valid for a generic function f and for any stochastic process.

If at this point one uses the conservation equation and the constitutive equations in the form used by Nadim *et al.*¹³ [their Eqs. (3.1) and (3.2)], which are nothing else than the approximate solution (called the P_1 approximation) of the Boltzmann equation in which one expands $f(\mathbf{r}, \mathbf{v}, t)$ in Legendre polynomials and truncates the series after two terms, the resulting expansion remains valid only for Markov processes in which the scattering medium has an isotropic velocity distribution in the laboratory reference system.

On the contrary, let us consider the Boltzmann equation which is also valid for any stochastic process because it is simply a detailed balance in the phase space. It reads, in its maximum generality,¹⁵

$$(\partial_t + \mathbf{v} \cdot \nabla + \mathbf{a} \cdot \nabla_{\mathbf{v}})f(\mathbf{r}, \mathbf{v}, t) = \int d^3 \mathbf{V} \int d^3 \mathbf{V}' \int d^3 \mathbf{v}' \{ \sigma(\mathbf{V}', \mathbf{v}' \rightarrow \mathbf{V}, \mathbf{v}) |\mathbf{v}' - \mathbf{V}'| F(\mathbf{r}, \mathbf{V}', t) f(\mathbf{r}, \mathbf{v}', t) - \sigma(\mathbf{V}, \mathbf{v} \rightarrow \mathbf{V}', \mathbf{v}') |\mathbf{v} - \mathbf{V}| F(\mathbf{r}, \mathbf{V}, t) f(\mathbf{r}, \mathbf{v}, t) \}, \quad (16)$$

where \mathbf{a} is the acceleration due to external fields, \mathbf{v} and \mathbf{v}' are the velocities before and after scattering, respectively, of the considered particle, and \mathbf{V} and \mathbf{V}' are those related to the scattering medium, the probability density of the latter in the phase space being $F(\mathbf{r}, \mathbf{V}, t)$. Moreover $\sigma(\mathbf{V}', \mathbf{v}' \rightarrow \mathbf{V}, \mathbf{v})$ is the scattering cross section for the transition from the primed to the nonprimed velocities. Usually the scattering medium is constituted by atoms or molecules but it can also be due to a random electromagnetic field, as that of stochastic electrodynamics or to the random bullets emitted by the considered rocket. For the molecules of a gas (or of a lattice of a solid) the probability density F is isotropic in the laboratory reference system. But for a non-Markov process F is generally nonisotropic and implies a memory. In the case of a stochastic motion with inertia (rocket emitting random bullets) F is isotropic with respect to the instantaneous velocity \mathbf{v} of the rocket. All this makes the solution of Eq. (16) extremely difficult for non-Markov processes. However, be-

cause of the reversibility of the microphysical elementary processes,

$$\sigma(\mathbf{V}', \mathbf{v}' \rightarrow \mathbf{V}, \mathbf{v}) = \sigma(\mathbf{V}, \mathbf{v} \rightarrow \mathbf{V}', \mathbf{v}')$$

and the integration over \mathbf{v} of the right-hand side of Eq. (16) (i.e., of the Boltzmann equation collision integral) vanishes if there is no variation of the total number of the particles.

In the case of sources (for example ionization) or of wells (for example electron attachment) the integration over \mathbf{v} gives simply $\alpha \rho(\mathbf{r}, t)$ where α is generation (ionization) or recombination (attachment) coefficient.

Let us therefore substitute the expansion (8) in Eq. (16) and integrate both sides over \mathbf{v} . The third term on the left-hand side of Eq. (16) generates, because of the gradient theorem, an integral over the boundary surface in the velocity space on which $f(\mathbf{r}, \infty, t) = 0$. Consequently we obtain, with the use of Eq. (1), and integrating over \mathbf{k} ,

$$\partial_t \rho(\mathbf{r}, t) - \sum_{n=0}^{\infty} \omega^{(n)} \odot^{(n)} \int d^3 \mathbf{r}' \frac{\sin[k_{Mx}(x-x')]}{\pi(x-x')} \frac{\sin[k_{My}(y-y')]}{\pi(y-y')} \frac{\sin[k_{Mz}(z-z')]}{\pi(z-z')} (-\nabla)^n \rho(\mathbf{r}', t) = 0, \quad (17)$$

where

$$\omega^{(n \geq 1)}(t) = \int d^3 \mathbf{v} \mathbf{v} \mathbf{Q}_{n-1}(\mathbf{v}, t) \quad \text{and} \quad \omega^{(0)} = -\alpha, \quad (18)$$

α being the defined decreasing coefficient (due, for instance, to recombination or electron attachment). When k_M is sufficiently large the first three factors inside the integral approximate the three-dimensional δ function and Eq. (17) becomes

$$\partial_t \rho(\mathbf{r}, t) - \sum_{n=0}^{\infty} \omega^{(n)}(t) \odot^{(n)} (-\nabla)^n \rho(\mathbf{r}, t) = 0. \quad (19)$$

We have thus obtained the desired density-gradient expansion (19), that is so proved in general for any stochastic process, although under limiting conditions. These are (i) The function $\rho(\mathbf{r}, t)$ must be continuous [while the more general expansion (17) is also valid for discontinuous functions]. (ii) If $\nabla \rho(\mathbf{r}, t)$ is large around a given \mathbf{r}' , the expansion (19) is valid only for $\mathbf{r} \sim \mathbf{r}'$. When it is valid with only $n=1$, the inclusion of the successive terms always improves the approximation because the two real series included in the complex series (6) have decreasing terms with alternating signs. This has been proved by simulation with a Monte Carlo Method for Markov processes, where the agreement appreciably improves¹⁶ up to $n \sim 5$ (then the results with $n=7$ are not appreciably different from those with $n=5$).

Our proof extend the validity of Eq. (19) to non-Markov processes (where there are no derivations and simulations), always under the above limitations (i) and (ii).

III. A GENERAL APPLICATION OF THE GRADIENT EXPANSION

Let us compare Eq. (19) with the continuity equation with source [which can be obtained by integrating Eq. (16) over \mathbf{v} without using the expansion (8)]

$$\partial_t \rho + \nabla \cdot [\rho \langle \mathbf{v} \rangle](\mathbf{r}, t) = -\alpha \rho, \quad (20)$$

where

$$\rho(\mathbf{r}, t) \langle \mathbf{v} \rangle(\mathbf{r}, t) = \int d^3 \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \mathbf{v} \quad (21)$$

defines the local average $\langle \mathbf{v} \rangle$ of the particle velocity \mathbf{v} . We get, since the $\omega^{(n)}$ do not depend on \mathbf{r} ,

$$\nabla \cdot (\rho \langle \mathbf{v} \rangle) - \rho \omega^{(1)} = \nabla \cdot \sum_{n=2}^{\infty} \omega^{(n)} \odot^{(n-1)} (-\nabla)^{(n-1)} \rho(\mathbf{r}, t) \quad (22)$$

whence

$$\rho[\langle \mathbf{v} \rangle - \omega^{(1)}] = \sum_{n=2}^{\infty} \omega^{(n)} \odot^{(n-1)} (-\nabla)^{(n-1)} \rho + \nabla \times \mathbf{A}(\mathbf{r}, t), \quad (23)$$

where $\mathbf{A}(\mathbf{r}, t)$ is an arbitrary vector and inside the square bracket there is the difference (which is a function of \mathbf{r} and t) between $\langle \mathbf{v} \rangle$ and the drift velocity $\omega^{(1)}$ which, by Eqs. (2) and (18), is given by

$$\omega^{(1)}(t) = \int d^3 \mathbf{v} f(\mathbf{v}, t) \mathbf{v}, \quad (24)$$

and is independent of \mathbf{r} . In some particular cases it is

$\nabla \times \mathbf{A} = 0$ so that Eq. (23) becomes, by explicitly writing the first three terms,

$$\rho[\langle \mathbf{v} \rangle - \omega^{(1)}] = -\omega^{(2)} \cdot \nabla \rho + \omega^{(3)} : \nabla \nabla \rho - \omega^{(4)} : \nabla \nabla \nabla \rho . \quad (25)$$

This is valid, for instance, in a Markovian process with an external uniform field in which the right-hand side represents the spreading due to diffusion. Indeed, in this case, Eq. (25) can be obtained by solving Boltzmann's relevant equation.

In a stationary process with a central force (for example because of a nucleus) it is $\langle \mathbf{v} \rangle = \omega^{(1)} = 0$, and $\nabla \times \mathbf{A}$

balances the whole series of ∇ in Eq. (23).

In an isotropic stochastic process it is

$$\omega^{(2)} = D_2 \boldsymbol{\eta} \quad \text{and} \quad \omega^{(3)} = \omega^{(5)} = \omega^{(7)} = \dots = 0 , \quad (26)$$

where D_2 is a constant scalar and $\boldsymbol{\eta}$ the fundamental tensor of the metric.

The most general expression for $\omega^{(4)}$, using its components, is

$$\omega_{ikrs} = D_a^{(4)} \eta_{ik} \eta_{rs} + D_b^{(4)} (\eta_{ir} \eta_{ks} + \eta_{is} \eta_{kr})$$

so that

$$\omega^{(4)} : \nabla \nabla \nabla \rho = [D_a^{(4)} \eta_k \eta_{rs} + D_b^{(4)} (\eta_r \eta_{ks} + \eta_s \eta_{kr})] \partial_k \partial_r \partial_s \rho = [D_a^{(4)} + 2D_b^{(4)}] \nabla \nabla^2 \rho = D_4 \nabla \nabla^2 \rho . \quad (27)$$

Consequently, Eq. (25) becomes

$$\rho[\langle \mathbf{v} \rangle - \omega^{(1)}] = -D_2 \nabla \rho - D_4 \nabla \nabla^2 \rho . \quad (28)$$

The two coefficients D_2 and D_4 can be obtained by solving the Boltzmann equation. Another equivalent way is the following. We take a sphere of radius λ , where λ is the mean free path, and then we calculate the net contribution of the number current density $\rho \mathbf{v}$ in the center of the sphere, due to the free flights, each coming from a point of the spherical surface where the number concentration (or probability density) is $\rho(\mathbf{r} - \lambda)$, where λ is parallel to the particle velocity and directly toward the center of the considered sphere. Using spherical coordinates the net contribution due to diffusion is

$$\mathbf{J}_D(\mathbf{v}) = \int_0^\pi \int_0^{2\pi} \frac{d\psi}{2\pi} \mathbf{v} \rho(\mathbf{r} - \lambda) , \quad (29)$$

where

$$\mathbf{v} = |\mathbf{v}| (\hat{\mathbf{i}} \sin \theta \cos \psi + \hat{\mathbf{j}} \sin \theta \sin \psi + \hat{\mathbf{k}} \cos \theta) , \quad (30)$$

and, by expanding ρ in a Taylor series

$$\rho(\mathbf{r} - \lambda) = \rho(\mathbf{r}) - \lambda \cdot \nabla \rho + \frac{1}{2} \lambda \lambda : \nabla \nabla \rho - \frac{1}{6} \lambda \lambda \lambda : \nabla \nabla \nabla \rho , \quad (31)$$

with

$$\lambda = \lambda \hat{\mathbf{v}} = \lambda (\hat{\mathbf{i}} \sin \theta \cos \psi + \hat{\mathbf{j}} \sin \theta \sin \psi + \hat{\mathbf{k}} \cos \theta) . \quad (32)$$

Substituting Eqs. (30), (31), and (32) in Eq. (29) gives, after easy but long calculations,

$$\mathbf{J}_D(\mathbf{r}, t) = -\frac{1}{3} \lambda v \nabla \rho - \frac{1}{30} \lambda^3 v \nabla \nabla^2 \rho . \quad (33)$$

Averaging Eq. (30) over the normalized distribution function $f(v)$ of the velocity magnitudes gives the second side of Eq. (28) with

$$D_2 = \int_0^\infty dv 4\pi v^2 f(v) \frac{1}{3} \lambda v , \quad (34)$$

$$D_4 = \int_0^\infty dv 4\pi v^2 f(v) \frac{1}{30} \lambda^3 v . \quad (35)$$

IV. A NON-MARKOVIAN STOCHASTIC EQUATION WHOSE LEADING TERMS COINCIDE WITH THE SCHRÖDINGER EQUATION

The diffusion current $\mathbf{J}_D(v)$ given by Eq. (33) is also valid for a non-Markovian process because it is simply the result of a net balance of flow inside a mean free path.

Locally, we can write

$$\rho \langle \mathbf{v}_1 \rangle = \mathbf{J}_{0_1} - D_2 \nabla \rho - D_4 \nabla \nabla^2 \rho , \quad (36)$$

where \mathbf{J}_{0_1} depends on the force fields and, in a process with inertia, on the preceding history, as well. The subscript 1 denotes the first considered volume element, for instance the little sphere of radius λ .

Let us now consider an adjacent small sphere (with subscript 2) having a radius λ . In a Markovian process we still have Eq. (36) with a very tiny variation due to the small displacement. In a motion with inertia the \mathbf{J}_{0_2} is equal to $\rho \langle \mathbf{v}_1 \rangle$ because the average effect due to the diffusion is remembered in the adjacent cell. If we now consider the almost local system constituted by the two adjacent cells, we have that the average velocity is

$$\rho \langle \mathbf{v}_{1,2} \rangle = \mathbf{J}_{0_1} - 1.5(D_2 \nabla \rho + D_4 \nabla \nabla^2 \rho) , \quad (37)$$

so that the ensemble average velocity with respect to this local center of mass is

$$\rho \langle \mathbf{v}_{\text{rel}} \rangle = \pm 0.5(D_2 \nabla \rho + D_4 \nabla \nabla^2 \rho) . \quad (38)$$

It would seem that Eqs. (37) and (38) would depend on the number of adjacent cells but if we only consider another, third cell, the coefficients D_2 and D_4 , which are calculated across a λ distance, would decrease. A mathematical proof of this intuitive assertion could be obtained from the Boltzmann equation considering the scattering centers as having an average local velocity equal to that of the considered particle.

Because of König's theorem, the local kinetic energy density U_k of the two adjacent cells is equal to that concentrated in the center of mass plus that relative to the center of mass

$$U_k = \frac{\rho}{2} (\langle \mathbf{v} \rangle^2 + \langle \mathbf{v}_{\text{rel}} \rangle^2). \quad (39)$$

In a motion with inertia we can write $\langle \mathbf{v} \rangle = \nabla \varphi$ (where φ is the velocity potential) and the equation of motion can be obtained by the stationarity of the action

$$\mathcal{A} = \int dt d^3r L, \quad (40)$$

where the Lagrangian density L is given by

$$L = \rho [\partial_t \varphi + V + \frac{1}{2} (\nabla \varphi)^2 + \frac{1}{2} \langle \mathbf{v}_{\text{rel}} \rangle^2], \quad (41)$$

in which V is the potential energy per unit mass and $\langle \mathbf{v}_{\text{rel}} \rangle$ is given by Eq. (38).

Let us set the functional derivative of \mathcal{A} with respect to φ equal to zero

$$\frac{\partial L}{\partial \varphi} - \partial_\alpha \left[\frac{\partial L}{\partial (\partial_\alpha \varphi)} \right] = 0, \quad (42)$$

where $\partial_\alpha = \partial / \partial x_\alpha$ with $\alpha = 0, 1, 2, 3$. In our case Eq. (42) reduces to

$$\begin{aligned} \frac{\partial \varphi}{\partial t} + \frac{1}{2} (\nabla \varphi)^2 + V + \frac{1}{4} D_2^2 \left[\frac{1}{2} \left(\frac{\nabla \rho}{\rho} \right)^2 - \frac{\nabla \rho}{\rho} \right] - \frac{1}{4\rho} \left[\frac{1}{2\rho} [D_4 \nabla (\nabla^2 \rho)]^2 + D_2 D_4 \nabla^2 \nabla^2 \rho \right] \\ - \frac{1}{4} \nabla^2 \left[\frac{1}{\rho} [D_2 D_4 \nabla^2 \rho - \frac{1}{\rho} D_2 D_4 (\nabla \rho)^2 + D_4^2 \nabla^2 \nabla^2 \rho - \frac{1}{\rho} D_4^2 \nabla \rho \cdot \nabla \nabla^2 \rho] \right] = 0. \end{aligned} \quad (46)$$

If we neglect the terms inside the curly brackets of Eq. (46), then the leading terms of Eq. (46) together with Eq. (44) coincide with Schrödinger's hydrodynamic equations. The terms inside the curly brackets of Eq. (46) can therefore be interpreted as correction terms to the Schrödinger equation.

In the new stochastic interpretation, quantum mechanics (QM) is nothing else than a classical motion with a superimposed stochastic jiggling motion with no friction and with a speed distribution function $f(v)$ independent of external forces, hence of time (*Zitterbewegung* assumption¹²). It follows that the two coefficients D_2 and D_4 given by Eqs. (34) and (35) are constant and such have been considered in deriving Eqs. (44) and (46). The simplest way to satisfy the *Zitterbewegung* assumption is to take it as given by the Schrödinger solution of the Dirac equation, which implies $v = c$ (where c is the speed of light), as particularly advocated by Barut.¹⁸ In this case, Eq. (34) gives

$$D_2 = \frac{1}{3} \lambda c. \quad (47)$$

If we drop the terms contained in the large parentheses in Eq. (46) we just get Schrödinger's second hydrodynamic equation if $D_2 = \hbar/m$. By this value and Eq. (47), the mean free path λ turns out to be

$$\partial_t \left[\frac{\partial L}{\partial (\partial_t \varphi)} \right] + \partial_s \left[\frac{\partial L}{\partial (\partial_s \varphi)} \right] = 0, \quad (43)$$

with $s = 1, 2, 3$. We obtain by Eqs. (41) and (43)

$$\partial_t \rho + \nabla \cdot (\rho \nabla \varphi) = 0, \quad (44)$$

which is the continuity equation expressing the conservation of the particles number. Setting the functional derivative of \mathcal{A} with respect to ρ equal to zero gives¹⁷

$$\begin{aligned} \frac{\partial L}{\partial \rho} - \partial_\alpha \left[\frac{\partial L}{\partial (\partial_\alpha \rho)} \right] + \partial_{\alpha\beta}^2 \left[\frac{\partial L}{\partial (\partial_{\alpha\beta} \rho)} \right] \\ - \partial_{\alpha\beta\gamma}^3 \left[\frac{\partial L}{\partial (\partial_{\alpha\beta\gamma} \rho)} \right] = 0, \end{aligned} \quad (45)$$

with $\alpha, \beta, \gamma = 0, 1, 2, 3$ although $[\partial L / \partial (\partial_0 \rho)] = 0$ because $\partial_0 \rho = \partial_t \rho$ does not appear in L given by Eq. (41). Notice that second- and third-order derivatives are here included because they appear in Eq. (38), which has to be inserted in Eq. (41). This is the improvement with respect to Ref. 12, where only $D_2 \nabla \rho$ is kept.

We obtain by Eqs. (41) and (45)

$$\lambda = \frac{3\hbar}{mc} = 6R_c, \quad (48)$$

where R_c is the Compton radius.¹⁹ By this value we get for D_4 as given by Eq. (35)

$$D_4 = \frac{1}{30} \lambda^3 c = \frac{9}{10} \frac{\hbar^3}{m^3 c^2}. \quad (49)$$

If we substitute Eqs. (47), (48), and (49) in Eq. (46) and apply Eqs. (44) and (46) to the fundamental state of a hydrogen atom, we find that the corrective terms in $D_2 D_4$ give contributions of the order $\alpha^2 = (e^2 / \hbar c)^2$, with respect to those obtainable by the fundamental terms [outside the large parentheses of Eq. (46)]. The terms in D_4^2 give relative corrections of order $\alpha^4 = (e^2 / \hbar c)^4$ and we can therefore drop them out of Eq. (46).

As is well known, it is more convenient, from the mathematical point of view, to solve a single complex equation instead of the system of two coupled equations. We have succeeded only in a partial way to obtain this goal. Indeed by the position

$$\psi = \rho^{1/2} \exp(i\varphi / 2D_2) \quad (50)$$

the following complex equation (where the D_4^2 terms have been dropped)

$$i\hbar\partial_t\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + m\psi \left\{ V - \frac{9}{40}\frac{\hbar^4}{m^4c^2} \left[\frac{1}{\rho}\nabla^2\nabla^2\rho + \nabla^2 \left(\frac{1}{\rho}\nabla^2\rho \right) - \nabla^2 \left(\frac{1}{\rho^2}(\nabla\rho)^2 \right) \right] \right\} \quad (51)$$

has the imaginary coefficient equal to Eq. (44) and the real part equal to Eq. (46).

Fortunately, the contribution coming from the terms in ρ in Eq. 51 is usually small with respect to that coming from the remanent part that is Schrödinger's standard equation. The latter can therefore be solved in the usual way for ψ , then $\rho = \psi/\psi^*$ is substituted in the corrective terms (classical perturbation method) that act as a small modification of the potential energy V per unit mass. Then Eq. (51) is solved again. The procedure can be repeated in an iterative way although, in usual cases, the additional terms in ρ give contributions of the order of the radiative corrections of quantum electrodynamics. It is to be inquired whether the *differences* of the corrections between the different modified atomic levels are detectable.

Certainly, the differences between the results obtainable from Eq. (51) and from the Schrödinger equation are very small in the case of stable states. The differences can be much higher in the case of scattering, where the corrective terms in $\nabla^2\nabla^2\rho$ of Eq. (51) are strongly enhanced when an electron passes very near either the nucleus or another electron of the atom. The problem could be similar to that of the flicker noise (or $1/\omega$ noise because its power spectral density is inversely proportional to the angular frequency ω). Indeed the "convective term," which is usually of the order of 10^{-4} compared to the Johnson-Nyquist leading term, can in a particular case become of the same order as the main term.²⁰ There is therefore the hope that the application of Eq. (51) can eliminate the 7% discrepancies between the experimental and theoretical values of the rotational cross sections between free electrons and hydrogen molecules.²¹ The ro-vibrational cross sections have a much higher threshold, implying higher energies for the impinging electrons and therefore closer approaches with consequent higher $\nabla^2\nabla^2\rho$ values. The corrective terms of Eq. (51) are therefore larger and, indeed, the discrepancies between the experimental values and those calculated by Schrödinger's usual equation are 50%. This standing problem has been discussed in a joint paper²¹ of Crompton (an experimentalist in this field) and Morrison (a theorist). We leave the formidable task of calculating the new values of the ro-vibrational cross sections between free electrons and hydrogen molecules obtainable from Eq. (51), to future work.

V. CONCLUSIONS

This paper has three achievements. (1) An integral expansion is obtained for the probability density $\rho(\mathbf{r}, t)$ in the ordinary space. The expansion is valid for a very wide class of ρ functions even noncontinuous and with large gradients, provided they are Fourier transformable.

Under the conditions (i) continuous ρ functions and (ii) $\nabla\rho$ small or, if large, only around the considered point \mathbf{r} , the integral expansion reduces to the usual density-gradient expansion whose field of validity is therefore well clarified.

(2) The extension of both expansions (integral and differential) to non-Markovian stochastic processes, i.e., to the processes whose stochastic environment has a memory. These are different from the Markovian nonhydrodynamic regime in which the electrons have a memory (for instance before reaching equilibrium with the external field) but the stochastic environment (molecules of the gas) is rigorously steady state and without any memory. This is reflected in the power spectral densities which are "colored" in non-Markovian processes and "white" (i.e., frequency independent below an upper cutoff) in the Markovian process.

(3) The application of the gradient expansion to the stochastic process with inertia, that is substantially equivalent to quantum electrodynamics (QED) and even foresees new phenomena, as the origin of the high-energy tail of the cosmic rays²² and the appearance of a friction in vacuo starting²³ from a high-energy threshold which, for a hydrogen atom, is 10^{13} eV.

The gradient expansion can also be found by a Taylor expansion of the probability density $\rho(\mathbf{r}, t)$ when one calculates the net diffusion flow in a spherical cell having a radius equal to the mean free path λ of the equivalent random walk. In a process with inertia, the net diffusion flow is remembered in the nearest-neighbor cell, where it is added to the average velocity of the preceding cell (because of all its preceding history). There is therefore an ensemble averaged-dispersion velocity with respect to the center of mass of the two adjacent cells. The corresponding kinetic energy U_k is remembered in a process with inertia (whereas it decays very quickly in a Markovian process) and is to be added to the kinetic energy of the center of mass (with the whole mass). The corresponding hydrodynamic equations derivable by a standard variational principle are those of Schrödinger if only two terms of the Taylor expansion are kept. Four terms are kept in this paper so that Eq. (51) is obtained, which is equivalent to the two hydrodynamic equations (44) and (46) and is more refined than Schrödinger equation.

The correction terms (with respect to the values obtainable from the Schrödinger equation) are of order α^2 (where α is the fine structure constant) for stable states. The correction terms should be greater for scattering problems and in particular when inelastic ro-vibrational cross sections are calculated. It is known²¹ that there are unexplainable differences for these cross sections between the experimental and theoretical values. There is therefore the hope that our correction terms may explain the differences and we leave the difficult task of calculating them by our Eq. (51) to future workers.

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