Particle-photon radiative interactions and thermalization

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We analyze the statistical properties of radiative transitions for a molecular system possessing discrete, equally spaced, energy levels, interacting with thermal radiation at constant temperature. A radiative fluctuation-dissipation theorem is derived and the particle velocity distribution analyzed. It is shown analytically that, neglecting molecular collisions, the velocity distribution function cannot be Gaussian, as the equilibrium value for the kurtosis κ is different from $\kappa = 3$. A Maxwellian velocity distribution can be recovered in the limit of small radiative friction.

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I. INTRODUCTION

One of the main contributions of quantum mechanics is the discovery that molecules possess an internal energy structure, owing to which they radiatively interact with the electromagnetic field via emission and absorption of energy quanta (photons) [1,2]. This phenomenon has a deep influence on the statistical and thermodynamic properties of molecular systems, as shown by Einstein, Debye, and many others [3,4], as regards both equilibrium and nonequilibrium properties. The theory of the specific heats of molecules (for instance, diatomic molecules) [5] and of solids [6] cannot be correctly framed without considering the quantum description of the excitations of the internal mechanical degrees of freedom.

The electromagnetic field, described by the system of the Maxwell equations, is responsible for mechanical actions in its interaction with material bodies (massive matter) due to momentum exchange (radiation pressure). This has been well known since Maxwell's time, and this currently finds important fields of applications in the study of condensed matter, in microtechnology and microfluidics, and in biology, as it is possible to manipulate mechanically micrometric particles, cells, and molecules through the use of light beams (optical tweezers) [7–9], focus particles at a given spatial location (optical traps) [10], or induce extreme thermal conditions in molecular assemblies via optical interactions (laser cooling techniques) [11–13].

Nevertheless, the most remarkable effect, as regards thermodynamic properties, is that the momentum exchange between matter and radiation (recoil effect) is the physical mechanism leading to thermalization. As shown by Einstein [14], considering exclusively radiative interactions between a molecular gas of identical molecules of mass m and thermal radiation at constant temperature T, the squared variance of the particle velocity entries $\langle v_i^2 \rangle$, $i = 1, 2, 3$, (since $\langle v_i \rangle = 0$) equals at equilibrium the Maxwellian result [4]

$$\langle v_i^2 \rangle = \frac{k_B T}{m}, \tag{1}$$

where k_B is the Boltzmann constant.

In this article we analyze the statistical properties of this interaction, formulating the problem in the form of a stochastic process over the increments of a Poisson counting process, applying the formalism recently proposed in [15] for stochastic chemical reactions. Extending the analysis to momentum transfer, we derive a radiative fluctuation-dissipation relation and the statistical properties of the particle velocities at equilibrium. Throughout this article we consider exclusively radiative interactions as regards particle momentum dynamics, deliberately neglecting the influence of particle-particle collisions. This choice has been made in order to enucleate and clarify the effects of the momentum exchange between particles and radiation on the statistical mechanical properties of a particle gas.

The properties of particle-particle collisions have been thoroughly addressed in [16,17] where the concept of conservative mixing transformations acting on a vector-valued ensemble was introduced in order to highlight the existence of an alternative distributional root to Gaussianity, completely different from the additive procedure of summation of random variables characteristic of the Central Limit Theory. In a physical perspective any thermalization process in a molecular gas is a consequence of the interplay between radiative processes and particle-particle collisions. We consider here only the first mechanism, since the sole presence of radiative effects is responsible for the achievement of an equilibrium velocity distribution characterized by a linear scaling equation (1) between the second-order velocity moments and temperature, even in the absence of significant collisional interaction. Therefore, the theory presented here applies to the case of extremely diluted particle gas systems in which the radiative emission-absorption processes are more frequent than binary collisional events. Despite the fact that radiative interactions

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provide the physical mechanism for thermalization, in the meaning of Eq. (1), the resulting velocity distributions deviate from the Maxwellian, and a Gaussian shape is recovered in the limit of small radiative friction. The analysis of light-matter interactions developed in this article is grounded on a stochastic modeling of the radiative events, and this is complementary to the statistical description based on the semiclassical evolution of the density matrix addressed in [18,19]. The advantage of the event-based formulation adopted in this article is that it not only provides the frequency of occupation of the energy level but it permits a simple description of the momentum transfer between energy quanta and matter, and thus the estimate of the equilibrium velocity distributions.

The article is organized as follows. Section II briefly introduces the problems and reviews the basic conservation principles that apply and the meaning of Einstein's result [14]. Section III develops the stochastic equations for the occupation numbers of the internal energy levels of a molecular system interacting with a given number of photons. We adopt the approximation of closed system discussed in [20], deriving the equilibrium properties. Section IV addresses the thermalization problem, i.e., the statistics of the momentum exchange between a particle gas and thermal radiation at constant temperature T. A new stochastic formulation of the particle equations of motion over the increments of a Poisson process is developed (the Appendix addresses some technicalities associated with this class of equations). A radiative fluctuation-dissipation theorem is formulated and the functional form of the velocity distribution function thoroughly considered in Sec. VII, showing its generic deviation from the Maxwellian behavior.

II. RADIATIVE INTERACTIONS

The interaction between a molecular system with radiation develops through (1) radiative processes of emission and absorption of radiation, (2) photon-molecule scattering, and (3) interactions with the zero-point energy field [21,22]. According to the analysis developed in [14], we neglect scattering processes, and the interactions with zero-point fluctuations, focusing exclusively on the effects of radiative transitions. Consider the transition of a quantum system (molecule) from the energy level E_1 to the energy level E_2 due to absorption of an energy quantum of frequency ν, with

$$E_2 - E_1 = h\,\nu, \tag{2}$$

where h is the Planck constant. This elementary event fulfils the fundamental principles of conservation of energy and momentum. Let $\mathbf{v}_1$ and $\mathbf{v}_2$ be the velocities of the molecule before and after the radiative interaction with the photon (in the present case an absorption event). Since a photon of energy $h\,\nu$ possesses a momentum $\mathbf{p}_\phi$ given by

$$\mathbf{p}_\phi = \frac{h\,\nu}{c}\,\mathbf{n}, \tag{3}$$

where c is the speed of light *in vacuo* and $\mathbf{n}$ the unit vector in the direction of propagation, in the low-velocity limit (so that relativistic corrections can be neglected), the energy balance reads

$$E_1 + \tfrac{1}{2} m\,|\mathbf{v}_1|^2 + h\,\nu = E_2 + \tfrac{1}{2}\,m\,|\mathbf{v}_2|^2, \tag{4}$$

where m is the mass of the molecule, and the momentum balance takes the form

$$m\,\mathbf{v}_1 + \frac{h\,\nu}{c}\,\mathbf{n} = m\,\mathbf{v}_2. \tag{5}$$

As the kinetic energy contributions are negligible, since using Eq. (5), Eq. (4) can be expressed as

$$E_1 + h\,\nu\,(1-\varepsilon) = E_2, \quad \varepsilon = \frac{2\,\mathbf{v}\cdot\mathbf{n}}{c} + \frac{h\,\nu}{m\,c^2}, \tag{6}$$

and ε is small in the nonrelativistic limit ($v/c \ll 1$), and for generic molecular systems ($h\nu/mc^2 \ll 1$), Eq. (4) can be simplified as

$$E_1 + h\,\nu = E_2. \tag{7}$$

As observed in [14], the radiative interactions, once considered in the reference frame of the moving particle, should account for relativistic corrections, specifically related to the property that the equilibrium spectral density of the radiation (the Planck distribution) is not Lorentz covariant. Once expressed in the reference frame of the molecule involved in the interaction, a dissipative term proportional to the ratio $\mathbf{v}_1/c$ arises in the momentum balance, so that Eq. (5) should be substituted by a dissipative dynamics, containing a friction term, the occurrence of which provides the equilibrium result (1); see also [4,23]. In the remainder of this paper we take this result for given, leaving to a future work a thorough and comprehensive discussion of the validity of momentum conservation in radiative processes.

III. THERMALIZATION OF INTERNAL QUANTUM STATES

Consider a system of identical molecules interacting with radiation through emission and absorption of energy quanta. For simplifying the analysis, the following assumptions are made:

(1) The molecules are characterized by a countable number of equally spaced energy levels E_k, with $E_{k+1} > E_k$, $k = 0, 1, \ldots,$ and

$$E_{k+1} - E_k = E_\delta = h\,\nu. \tag{8}$$

(2) The molecules interact with a photon gas at thermal equilibrium with temperature T.

(3) The system is closed and isolated, as regards both molecules and photons.

The last assumption simplifies the analysis but does not alter the physics of the problem and the results obtained at equilibrium.

Let $p_k(t)$ be the number density in the occupation of the k level at time t, p_k^0 its initial value at time $t = 0$, $q(t)$ the density of photons at the resonant frequency ν, and q^0 its initial value. Mass conservation implies that

$$\sum_{k=0}^{\infty} p_k(t) = \sum_{k=0}^{\infty} p_k^0 = P_{\rm tot}. \tag{9}$$

As the system is supposed to be isolated, i.e., closed with respect to radiation, the principle of conservation of the "virtual photon number" applies, dictating that

$$q(t) + \sum_{k=1}^{\infty} k\, p_k(t) = q^0 + \sum_{k=0}^{\infty} k\, p_k^0. \tag{10}$$

The interaction of the molecules with the photon gas implies the emission or absorption of radiation, where the emission process can be either a spontaneous or a stimulated transition, i.e., induced by a collision with an incoming photon. Therefore, if λ is the emission rate, we have

$$\lambda = \lambda_s + \lambda_0\, q(t), \tag{11}$$

where λ_s is the rate of spontaneous emission, while the absorption rate μ is given by

$$\mu = \mu_0\, q(t). \tag{12}$$

As shown by Einstein [14], the specific rate of absorption and stimulated emission should be equal:

$$\mu_0 = \lambda_0. \tag{13}$$

Consider for simplicity transition processes among nearest-neighboring energy levels. The inclusion of higher-order transitions does not add any new physics, making solely the notation more complicated and lengthy. The balance equations for this process read

$$\begin{aligned}\frac{dp_k(t)}{dt} &= -\{[\lambda_s + \lambda_0 q(t)]\, \eta_k + \lambda_0\, q(t)\}\, p_k(t) \\ &\quad + [\lambda_s + \lambda_0\, q(t)]\, p_{k+1}(t) + \lambda_0\, q(t)\, p_{k-1}(t),\end{aligned} \tag{14}$$

$k = 0, 1, \dots,$ where $\eta_0 = 0$, $\eta_k = 1$ for $k = 1, 2, \dots,$ and $p_{-1} = 0$, and

$$\frac{dq(t)}{dt} = [\lambda_s + \lambda_0\, q(t)] \sum_{k=1}^{\infty} p_k(t) - \lambda_0\, q(t) \sum_{k=0}^{\infty} p_k(t). \tag{15}$$

In a stochastic representation of the process, let $N_k(t)$ be the number of molecules in the kth level, and $N^q(t)$ the photon number. If N_g is the granularity number chosen [15], $\sum_{k=0}^{\infty} N_k(0) = N_g$, the relations between $N_k(t)$ and $p_k(t)$ and between $q(t)$ and $N^q(t)$ are expressed by

$$p_k(t) = P_{\text{tot}} \frac{N_k(t)}{N_g}, \quad q(t) = P_{\text{tot}} \frac{N^q(t)}{N_g}. \tag{16}$$

Expressed in terms of $N_k(t)$, $N^q(t)$, the balance equations (14) and (15) thus become

$$\begin{aligned}\frac{dN_k(t)}{dt} &= -\left\{[\widetilde{\lambda}_s + \widetilde{\lambda}_0 N^q(t)]\, \eta_k + \widetilde{\lambda}_0\, N^q(t)\right\} N_k(t) \\ &\quad + [\widetilde{\lambda}_s + \widetilde{\lambda}_0\, N^q(t)]\, N_{k+1}(t) + \widetilde{\lambda}_0\, N^q(t)\, N_{k-1}(t), \\ \frac{dN^q(t)}{dt} &= [\widetilde{\lambda}_s + \widetilde{\lambda}_0\, N^q(t)] \sum_{k=1}^{\infty} N_k(t) - \widetilde{\lambda}_0\, N^q(t) \sum_{k=0}^{\infty} N_k(t),\end{aligned} \tag{17}$$

with

$$\widetilde{\lambda}_s = \lambda_s, \quad \widetilde{\lambda}_0 = \lambda_0 \frac{P_{\text{tot}}}{N_g}. \tag{18}$$

A stochastic Markovian dynamics follows from Eqs. (17) and (18), applying the formalism developed in [15], by considering as stochastic variables the energy state of each molecule and $N^q(t)$. Let $\sigma_\alpha(t) = 0, 1, \dots$ be the energy state of the αth molecule at time t, $h = 1, \dots, N_g$. The evolution of $\{\sigma_\alpha(t)\}_{\alpha=1}^{N_g}$ follows the Markovian dynamics,

$$\begin{aligned}\frac{d\sigma_\alpha(t)}{dt} &= -\eta_{\sigma_\alpha(t)} \frac{d\chi_\alpha^{(e)}(t, \widetilde{\lambda}_s + \widetilde{\lambda}_0\, N^q(t))}{dt} \\ &\quad + \frac{d\chi_\alpha^{(a)}(t, \widetilde{\lambda}_0\, N^q(t))}{dt},\end{aligned} \tag{19}$$

while

$$\begin{aligned}\frac{dN^q(t)}{dt} &= \sum_{\alpha=1}^{N_g} \eta_{\sigma_\alpha(t)} \frac{d\chi_\alpha^{(e)}(t, \widetilde{\lambda}_s + \widetilde{\lambda}_0\, N^q(t))}{dt} \\ &\quad - \sum_{\alpha=1}^{N_g} \frac{d\chi_\alpha^{(a)}(t, \widetilde{\lambda}_0\, N^q(t))}{dt},\end{aligned} \tag{20}$$

where $\{\chi_\alpha^{(e)}(t, \widetilde{\lambda}_s + \widetilde{\lambda}_0\, N^q(t))\}_{\alpha=1}^{N_g}$ and $\{\chi_\alpha^{(a)}(t, \widetilde{\lambda}_0\, N^q(t))\}_{\alpha=1}^{N_g}$ are two families of N_g independent Poisson counting processes, mutually independent of each other, associated with the emission and absorption events of the αth molecules. Observe that the transition rates of these processes depend explicitly on the photon number $N^q(t)$.

Given $\{\sigma_\alpha(t)\}_{\alpha=1}^{N_g}$, the occupation number $N_k(t)$ of the kth energy level is given by

$$N_k(t) = \sum_{\alpha=1}^{N_g} \delta_{k,\sigma_\alpha(t)}, \tag{21}$$

where δ_{k,σ_α} are the Kronecker symbols, so that $\delta_{k,\sigma_\alpha(t)} = 1$ if $\sigma_\alpha(t) = k$, and zero otherwise.

Consider the equilibrium properties of this system, indicating with p_k^* and q^* the equilibrium values. Equation (14) for $k = 0$ at steady state becomes

$$-\lambda_0\, q^*\, p_0^* + (\lambda_s + \lambda_0\, q^*)\, p_1^* = 0, \tag{22}$$

so that

$$p_1^* = \frac{\lambda_0\, q^*}{\lambda_s + \lambda_0\, q^*}\, p_0^*. \tag{23}$$

An analogous relation applies for generic $k = 1, 2, \dots,$ namely,

$$p_{k+1}^* = \frac{\lambda_0\, q^*}{\lambda_s + \lambda_0\, q^*}\, p_k^*. \tag{24}$$

Therefore, as expected, the equilibrium distribution of level occupation is given by

$$p_h = C \left(\frac{\lambda_0\, q^*}{\lambda_s + \lambda_0\, q^*} \right)^h = C\, \exp\left[-h\, \log\left(\frac{\lambda_s + \lambda_0\, q^*}{\lambda_0\, q^*} \right) \right]. \tag{25}$$

It is a discrete Boltzmann distribution, where the term $\log((\lambda_s + \lambda_0\, q^*)/\lambda_0\, q^*)$ can be identified with the Boltzmann factor $E_\delta / k_B\, T$,

$$\frac{E_\delta}{k_B\, T} = \log\left(\frac{\lambda_s + \lambda_0\, q^*}{\lambda_0\, q^*} \right), \tag{26}$$

and this provides an alternative definition of equilibrium temperature T based on radiative interactions

$$T = \frac{E_\delta}{k_B} \frac{1}{\log\left(\frac{\lambda_s+\lambda_0 q^*}{\lambda_0 q^*}\right)}. \tag{27}$$

From Eq. (27), temperature is uniquely specified, once the equilibrium photon density q^* is given. Consequently for radiative processes the equilibrium temperature is one-to-one with the steady-state value of the photon density q^*. Two limit cases can be considered. For $\lambda_s \gg \lambda_0 q^*$, i.e., for low photon densities, Eq. (26) simplifies as

$$\log\left(\frac{\lambda_s}{\lambda_0 q^*}\right) = \frac{E_\delta}{k_B T}, \quad \Rightarrow \quad q^* = \frac{\lambda_s}{\lambda_0} e^{-h\nu/k_B T}. \tag{28}$$

In the opposite case, $\lambda_s \ll \lambda_0 q^*$, i.e., in the high photon-density limit,

$$\log\left(1 + \frac{\lambda_s}{\lambda_0 q^*}\right) \simeq \frac{\lambda_s}{\lambda_0 q^*} = \frac{E_\delta}{k_B T}, \tag{29}$$

and thus the equilibrium photon density q^* is proportional to the temperature T:

$$q^* = \frac{k_B T}{h\nu} \frac{\lambda_s}{\lambda_0}. \tag{30}$$

Next, consider the expression for q^*. Set $\lambda = \lambda_s + \lambda_0 q^*$, and $\mu = \lambda_0 q^*$, for notational simplicity, and $x = \mu/\lambda < 1$, so that the equilibrium occupational distribution can be expressed compactly as $p_k^* = C x^k$. The conditions expressed by Eqs. (9) and (10) become at equilibrium

$$\sum_{k=0}^{\infty} p_k^* = P_{\text{tot}} \tag{31}$$

and

$$q^* + \sum_{k=1}^{\infty} h\, p_k^* = q^0 + \sum_{k=1}^{\infty} p_k^0 = \Phi_0. \tag{32}$$

Since $\sum_{k=0}^{\infty} x^k = \frac{1}{1-x}$, $\sum_{k=1}^{\infty} k\, x^k = \frac{x}{(1-x)^2}$, we have for the normalization constant C,

$$C = P_{\text{tot}}\,(1-x), \tag{33}$$

and Eq. (32) becomes

$$\Phi_0 - q^* = P_{\text{tot}} \frac{x}{1-x}, \tag{34}$$

which can be explicated with respect to q^* to provide

$$q^* = \frac{\Phi_0}{1 + \frac{\lambda_0}{\lambda_s} P_{\text{tot}}}. \tag{35}$$

Figure 1 depicts the evolution of $q(t)$ obtained from stochastic simulations at $\lambda_0 = 10^{-3}$ for different values of λ_s. In the simulations we have chosen $P_{\text{tot}} = 10$, and the initial conditions are $p_k^0 = 10\,\delta_{k,10}$, corresponding to an initial population in the 10th excited state. The stochastic simulations refer to a granularity number $N_g = 10^4$, and 100 energy levels have been considered. The steady-state distributions of the occupation of the energy levels are depicted in Fig. 2 for the same values of the parameters of Fig. 1. From the long-term behavior of $q(t)$, the equilibrium value q^* can be obtained.

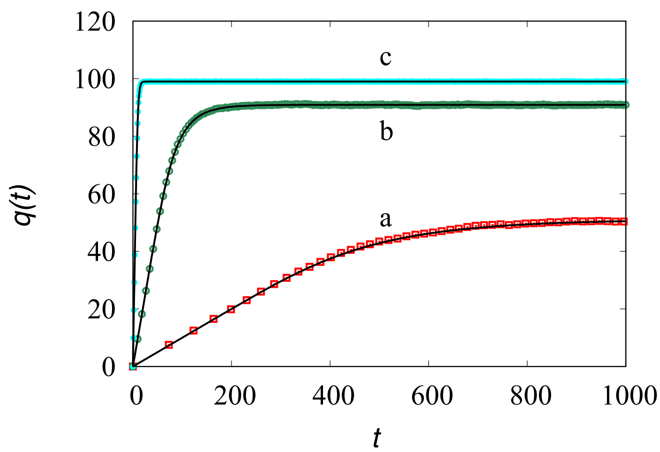

FIG. 1. $q(t)$ vs t for different values of λ_s: symbols are the results of stochastic simulations (19) and (20), lines correspond to the solution of the continuous model. Line a: $\lambda_s = 0.01$; line b: $\lambda_s = 0.1$; line c: $\lambda_s = 1$.

This is depicted in Fig. 3 as a function of λ_s. Finally, Fig. 4 depicts the value of the scaling exponent ζ of p_k^*, $p_k^* = Ce^{-k\zeta}$ obtained for the data of Fig. 2, compared to the theoretical expression $\zeta = \log[(\lambda_s + \lambda_0 q^*)/\lambda_0 q^*]$, revealing the excellent agreement of the stochastic simulations with the theoretical values.

IV. IMPLICATIONS OF RADIATIVE EVENTS IN THE VELOCITY STATISTICS

From the work by Einstein on emission and absorption of radiation [14] it becomes clear that thermalization processes, i.e., the relaxation of a physical system far from equilibrium towards the thermal equilibrium, could be considered as quantum effects driven by emission and absorption of energy quanta.

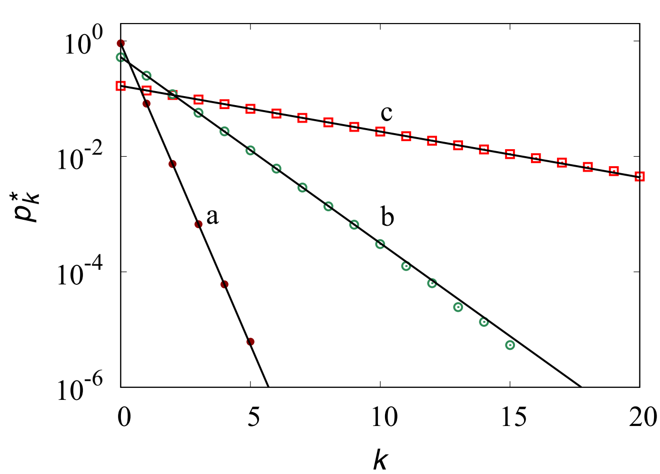

FIG. 2. p_k^* vs k for different values of λ_s: symbols are the results of stochastic simulations (19) and (20), lines correspond to the exponential (Boltzmann) distribution (25) with q^* given by Eq. (35). Line a: $\lambda_s = 0.01$; line b: $\lambda_s = 0.1$; line c: $\lambda_s = 1$.

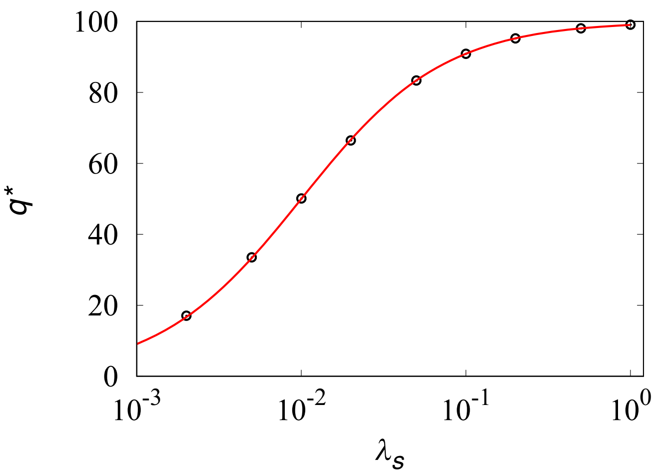

FIG. 3. q^* vs λ_s for $\lambda_0 = 10^{-3}$, $P_{\text{tot}} = 10$, $\phi_0 = 100$. Symbols ($\circ$) are the results of the stochastic simulations (with $N_g = 10^4$), line corresponds to Eq. (35).

This is certainly the case of a diluted gas of massive particles (molecules) interacting with thermal radiation (i.e., a photon gas at thermal equilibrium, the statistical properties of which are described by the Planck distribution), in which the following assumptions can be made:

(1) Particle dynamics is characterized by two main interactions: (1) emission and absorption of energy quanta by a particle and (2) particle-particle collisions. The assumption of "diluted system" indicates that solely binary collisions are relevant.

(2) These two processes can be considered as instantaneous events characterized by a Markovian transition structure.

(3) Between two subsequent events (be they particle-photon radiative interactions or particle-particle collisions), the particle motion is purely inertial, i.e., frictionless and in the absence of external or interparticle potentials.

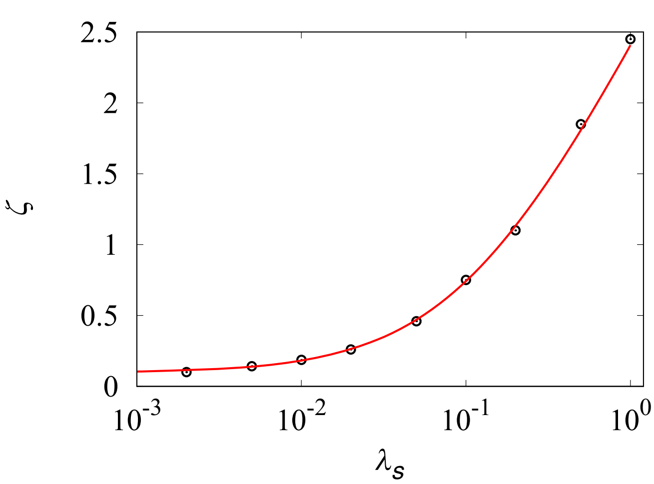

FIG. 4. Exponent ζ vs λ_s for $\lambda_0 = 10^{-3}$, $P_{\text{tot}} = 10$, $\phi_0 = 100$. Symbols ($\circ$) are the results of the stochastic simulations (with $N_g = 10^4$), line corresponds to the theoretical expression obtained from the continuous model.

Moreover, relativistic corrections determine the emergence of a dissipative term in the momentum dynamics proportional to the velocity of the molecule. Let us further assume that the particles (molecules) can be represented by a two-level system, where E_1 and E_2 are the two energy levels $E_2 > E_1$ and $E_2 - E_1 = h\,\nu$.

In this section we consider exclusively particle-photon radiative interactions and their effects on momentum transfer and velocity statistics, leaving the interplay between radiative processes and mechanical collisions to a subsequent analysis.

Following the assumptions discussed above, the momentum equation for a generic particle, due to the radiative interactions, can be described by means of the stochastic differential equation

$$m\,\frac{d\mathbf{v}}{dt} = (-\eta\,\mathbf{v} + \mathbf{b})\,\frac{d\chi(t,\lambda)}{dt}, \tag{36}$$

where m is the particle mass, and $\mathbf{v}$ its velocity vector. The coefficient η is the *radiative friction factor*, possessing the dimension of a mass. As addressed in Einstein's work [14], the radiative friction is an emergent property of the momentum exchange between a molecule and a photon during the radiative process (be it emission or absorption), related to the well-known recoil effect. In Eq. (36), $\chi(t,\lambda)$ is a Poisson process possessing transition rate λ, and $\mathbf{b}$ is a random variable corresponding to the photon momentum.

Equation (36) is a nonlinear impulse-driven stochastic differential equation [24–27]. Just because of the presence of the factor $-\eta\,\mathbf{v}$ multiplying the distributional derivative of the Poisson counting process, the proper mathematical setting of this class of equations requires some caution, as addressed in the Appendix. In point of fact, there is a strong analogy between the mathematical formalization of this class of impulse-driven stochastic differential equations and the setting of nonlinear Wiener-driven Langevin equations, leading to the Itô, Stratonovich, and Hänggi-Klimontovich formulations [28,29].

It is important to notice that Eq. (36) corresponds to an impulsive description of momentum transfer in which even the radiative dissipation acts impulsively, consistently with the instantaneous description of elementary quantum events in a stochastic formalism [30]. Consequently, the statistical properties associated with Eq. (36) find no direct counterpart with the stochastic description widely used in statistical mechanics in which dissipation is due to the steadily interaction with the surrounding fluid, and thus is described as a continuous process as in the classical Langevin equations [31,32]. It is therefore not surprising that the equilibrium distributions associated with the impulsive process Eq. (36) may deviate from the Gaussian paradigm characterizing Langevin equations driven by Wiener processes.

In order to avoid confusion, even in the case of collision-driven momentum exchange, the occurrence of Gaussianity in the velocity distributions has nothing to do with the implications of the Central Limit Theorem (CLT) [33], as thoroughly addressed in [16,17]. This stems from the fact that for non-relativistic elastic collisions the squared norm of the velocity is conserved, while CLT imples an additive route in which a system of stochastic contributions provide the divergence for the squared variance of the resulting sum. The latter mechanism clearly explains the emergence of the diffusion equation from stochastic random motion, but it is not suited for providing a cogent mathematical model for the collisional momentum transfer. For this reason in [16,17] the concept of conservative mixing transformations in a random ensemble has been introduced as the distributive route to Gaussianity alterative to the additive CLT route.

V. MOMENTUM TRANSFER AND RADIATIVE FLUCTUATION-DISSIPATION RELATIONS

Equation (36) describes the momentum transfer in a radiative process. Let $t = t^*$ be a time instant at which $\chi(t, \lambda)$ exhibits a transition, so that in the neighborhood of t^* Eq. (36) is equivalent to

$$m \frac{d\mathbf{v}}{dt} = (-\eta\, \mathbf{v} + \mathbf{b})\, \delta(t - t^*). \tag{37}$$

Integrating the latter equation between t_-^* and t_+^*, and letting $\mathbf{v} = \mathbf{v}(t_-^*)$, $\mathbf{v}' = \mathbf{v}'(t_+^*)$, $\mathbf{b} = \mathbf{b}(t^*)$, we have (see the Appendix)

$$\mathbf{v}' = e^{-\eta/m}\, \mathbf{v} + \frac{\mathbf{b}}{\eta}\, (1 - e^{-\eta/m}), \tag{38}$$

where $\eta = m\,\gamma$, so that γ is nondimensional, $\mathbf{b} = b\,\mathbf{r}$, where $b = h\,\nu/c$, corresponding to the norm of the momentum of a photon with energy $h\,\nu$, and $\mathbf{r}$ is a unit random vector, $|\mathbf{r}| = 1$, $\langle \mathbf{r} \rangle = 0$, where $\langle \cdot \rangle$ is the average with respect to the probability measure of $\mathbf{r}$. Thus,

$$\mathbf{v}' = \alpha\, \mathbf{v} + \frac{b\, \mathbf{r}\, (1 - \alpha)}{\eta}, \tag{39}$$

where $\alpha = e^{-\gamma}$. Since it is reasonable to assume the absence of correlation (independence) between the particle velocity $\mathbf{v}$ and the direction $\mathbf{r}$ of the incoming or emitted photon (this is certainly true for absorption and spontaneous emission, and it can be extrapolated also in the case of stimulated emission since particle velocity and the direction of the incoming photon are certainly uncorrelated from each other), it follows from Eq. (39) that

$$\langle |\mathbf{v}'|^2 \rangle = \alpha^2\, \langle |\mathbf{v}|^2 \rangle + \frac{b^2\, (1 - \alpha)^2}{\eta^2}. \tag{40}$$

Enforcing at thermal equilibrium the condition $\langle |\mathbf{v}'|^2 \rangle = \langle |\mathbf{v}|^2 \rangle = 3\, k_B\, T/m$, we have

$$3\, \frac{k_B\, T}{m}\, (1 - \alpha^2) = \frac{b^2\, (1 - \alpha)^2}{\eta^2}. \tag{41}$$

Equation (41) represents the first radiative fluctuation-dissipation relation, connecting the nondimensional friction factor γ to the equilibrium temperature T.

In the limit for $\gamma \ll 1$, $e^{-\gamma} \simeq 1 - \gamma$, and Eq. (41) reduces to

$$6\, \frac{k_B\, T}{m}\, \gamma = \frac{b^2}{m^2} \quad \Rightarrow \quad \gamma = \frac{(h\, \nu)^2}{6\, m\, c^2\, k_B\, T}, \tag{42}$$

which, setting $E_\phi = h\,\nu$, $E_0 = m\, c^2$, $E_T = k_B\, T$ can be rewritten in a more compact way as

$$\gamma = \frac{E_\phi^2}{6\, E_0\, E_T}. \tag{43}$$

Equation (43) indicates that, in the low-friction limit, the nondimensional radiative friction γ is proportional to the ratio of the squared photon energy to the product of the particle rest energy E_0 times the characteristic thermal energy E_T.

The momentum dynamics can be naturally expressed with respect to the operational time $n = 0, 1, 2, \ldots$ corresponding to the number of radiative events occurred, as

$$\mathbf{v}_{n+1} = \alpha\, \mathbf{v}_n + \beta\, \mathbf{r}_{n+1}, \tag{44}$$

where $\beta = b\,(1 - \alpha)/\eta$, and $\mathbf{r}_{n+1}$ is a family of vector-valued independent unit random vectors, uniformly distributed on the surface of the unit sphere. Equation (44) can be viewed as an iterated function system [34] with a continuous systems of linear contractive transformations. The discrete dynamics Eq. (44) can be explicated

$$\mathbf{v}_n = \alpha^n\, \mathbf{v}_0 + \beta \sum_{j=1}^{n} \alpha^{n-j}\, \mathbf{r}_j. \tag{45}$$

In the long-term limit, the first term, $\alpha^n\, \mathbf{v}_0$, depending on the initial velocity condition, can be ignored as it decays exponentially to zero, so that

$$\mathbf{v}_n = \beta \sum_{j=1}^{n} \alpha^{n-j}\, \mathbf{r}_j. \tag{46}$$

Consider the correlation tensor $\langle \mathbf{v}_n \otimes \mathbf{v}_p \rangle$, with $p \leqslant n$,

$$\langle \mathbf{v}_n \otimes \mathbf{v}_p \rangle = \beta^2 \sum_{j=1}^{n} \sum_{k=1}^{p} \alpha^{n+p-j-k} \langle \mathbf{r}_j \otimes \mathbf{r}_k \rangle. \tag{47}$$

In the 3D space, enforcing the independence of $\mathbf{r}_j$ and $\mathbf{r}_k$ for $j \neq k$, and the uniformity of the distribution on the surface of the unit sphere, we have

$$\langle \mathbf{r}_j \otimes \mathbf{r}_k \rangle = \frac{\delta_{j,k}\, \mathbf{I}}{3}, \tag{48}$$

where $\mathbf{I}$ is the identity matrix, so that Eq. (47) becomes

$$\langle \mathbf{v}_n \otimes \mathbf{v}_p \rangle = \frac{\beta^2\, \mathbf{I}}{3}\, \alpha^{n+p} \sum_{k=1}^{p} \alpha^{-2\,k}. \tag{49}$$

Making use of the elementary property

$$\sum_{k=1}^{p} \alpha^{-2\,k} = \frac{\alpha^{-2} - \alpha^{-2\,(p+1)}}{1 - \alpha^{-2}}. \tag{50}$$

Equation (49) can be rewritten as

$$\langle \mathbf{v}_n \otimes \mathbf{v}_p \rangle = \frac{\widetilde{\beta}^2\, \mathbf{I}\, \alpha^{n+p}}{3} \left(\frac{\alpha^{-2} - \alpha^{-2\,(p+1)}}{1 - \alpha^{-2}} \right). \tag{51}$$

In the long-term limit $n, p \to \infty$ (with $n - p$ finite), we obtain

$$\langle \mathbf{v}_n \otimes \mathbf{v}_p \rangle = \frac{\beta^2}{3}\, \mathbf{I}\, \frac{\alpha^{n-p}}{1 - \alpha^2} = \frac{\beta^2}{3\,(1 - \alpha^2)}\, \mathbf{I}\, e^{-(n-p)\, \log(1/\alpha)}. \tag{52}$$

The latter result can be expressed with respect to the physical time t, as $(n - p) = t/\langle \tau \rangle$, where $\langle \tau \rangle = 1/\lambda$ corresponds to the mean transition time. This leads to the expression for the velocity autocorrelation tensor,

$$\langle \mathbf{v}(t+\tau) \otimes \mathbf{v}(\tau) \rangle = \frac{\beta^2 \, e^{-\eta_r \, t/m}}{3\,(1-\alpha^2)} \, \mathbf{I}, \tag{53}$$

corresponding to an exponential decay with time t, where the effective radiative dissipation factor η_r is defined by the relation

$$\eta_r = m \, \lambda \, \log\left(\frac{1}{\alpha}\right). \tag{54}$$

The effective diffusivity D can be derived from the extension of the Einstein fluctuation-dissipation relation to radiative processes, $D \, \eta_r = k_B \, T$, to obtain

$$\frac{k_B \, T}{m \, D} = \lambda \, \log\left(\frac{1}{\alpha}\right). \tag{55}$$

In the limit of small $\gamma \ll 1$, $\alpha = 1 - \gamma$, and thus

$$D = \frac{k_B \, T}{m \, \lambda \, \log\left(\frac{1}{1-\gamma}\right)}, \tag{56}$$

which can be viewed as the second radiative fluctuation-dissipation relation connecting the effective diffusivity D to the statistics of radiative events.

VI. STATISTICAL CHARACTERIZATION OF THE VELOCITY DISTRIBUTION FUNCTION

In this section we consider the statistical properties of particle velocities emerging from purely radiative interactions with an equilibrium photon bath. To this end, it is convenient to discuss separately the 2D case from the 3D situation. Rescaling the velocity variables $\mathbf{v} \mapsto \mathbf{v}/\sigma_{\text{ph}}$, with respect to the variance of the photon forcing term σ_{ph},

$$\sigma_{\text{ph}} = \frac{\beta}{\sqrt{d}}, \tag{57}$$

where $d = 2, 3$, the rescaled equation attains the simple form

$$\mathbf{v}' = \alpha \, \mathbf{v} + \sqrt{d} \, \mathbf{r}, \tag{58}$$

where the random vector $\mathbf{r}$ is defined, in two dimensions, as

$$\mathbf{r} = \begin{pmatrix} \cos\phi \\ \sin\phi \end{pmatrix} \tag{59}$$

with a uniform probability density function $p_\phi(\phi)$,

$$p_\phi(\phi) = \frac{1}{2\,\pi}, \quad \phi \in [0, 2\,\pi], \tag{60}$$

while in the 3D case

$$\mathbf{r} = \begin{pmatrix} \sin\theta \, \cos\phi \\ \sin\theta \, \sin\phi \\ \cos\theta \end{pmatrix} \tag{61}$$

with a joint probability density function $p_{\theta,\phi}(\theta, \phi)$

$$p_{\theta,\phi}(\theta, \phi) = \frac{\sin\theta}{4\,\pi}, \quad (\theta, \phi) \in [0, \pi] \times [0, 2\pi]. \tag{62}$$

Owing to isotropy, in the 2D case it is sufficient to consider the 1D velocity dynamics

$$v' = \alpha \, v + \sqrt{2} \, \cos\phi, \quad p_\phi(\phi) = \frac{1}{2\,\pi}, \quad \phi \in [0, 2\,\pi], \tag{63}$$

and similarly in the 3D case, the equivalent 1D model becomes

$$v' = \alpha \, v + \sqrt{3} \, \cos\theta, \quad p_\theta(\theta) = \frac{\sin\theta}{2}, \quad \theta \in [0, \pi]. \tag{64}$$

To begin with, consider the 2D case, for which

$$\langle \cos^2\phi \rangle = \tfrac{1}{2}, \quad \langle \cos^4\phi \rangle = \tfrac{3}{8}. \tag{65}$$

Therefore, at equilibrium $\langle v \rangle = 0$, and

$$\langle v^2 \rangle = \alpha^2 \, \langle v^2 \rangle + 1, \tag{66}$$

i.e.,

$$\langle v^2 \rangle = \frac{1}{1-\alpha^2}. \tag{67}$$

As regards the qualitative statistical properties, the main issue is the deviation from a Gaussian behavior. For this reason, it is interesting to consider the fourth-order moment and, out of it, the kurtosis. Enforcing the independence between v and ϕ random variables, the fourth-order moment takes the form

$$\langle v^4 \rangle = \langle (\alpha \, v + \sqrt{2} \, \cos\phi)^4 \rangle = \alpha^4 \, \langle v^4 \rangle + 6\,\alpha^2 \, \langle v^2 \rangle + \tfrac{3}{2} \tag{68}$$

so that

$$\langle v^4 \rangle = \frac{3\,(1+3\,\alpha^2)}{2\,(1-\alpha^2)\,(1-\alpha^4)}. \tag{69}$$

From Eqs. (67) and (69) the expression for the kurtosis $\kappa(\alpha)$ follows:

$$\kappa(\alpha) = \frac{\langle v^4 \rangle}{\langle v^2 \rangle^2} = \frac{3\,(1+3\,\alpha^2)\,(1-\alpha^2)^2}{2\,(1-\alpha^2)\,(1-\alpha^4)} = \frac{3\,(1+3\,\alpha^2)}{2\,(1+\alpha^2)}. \tag{70}$$

A Gaussian behavior is expected for $\alpha \to 1$, since

$$\lim_{\alpha\to 1} \kappa(\alpha) = 3. \tag{71}$$

Next, consider the 3D case, for which

$$\langle \cos^2\theta \rangle = \tfrac{1}{3}, \qquad \langle \cos^4\theta \rangle = \tfrac{1}{5}. \tag{72}$$

Also in this case $\langle v \rangle = 0$ and $\langle v^2 \rangle$ is given by Eq. (67). As regards the fourth-order moment, we have

$$\langle v^4 \rangle = \langle (\alpha \, v + \sqrt{3} \, \cos\theta)^4 \rangle = \alpha^4 \, \langle v^4 \rangle + 6\,\alpha^2 \, \langle v^2 \rangle + \tfrac{9}{5}, \tag{73}$$

and therefore,

$$\langle v^4 \rangle = \frac{21\,\alpha^2 + 9}{5\,(1-\alpha^2)\,(1-\alpha^4)}. \tag{74}$$

Consequently, the kurtosis is given by

$$\kappa(\alpha) = \frac{(21\,\alpha^2+9)\,(1-\alpha^2)}{5\,(1-\alpha^4)} = \frac{3\,(3+7\,\alpha^2)}{5\,(1+\alpha^2)}. \tag{75}$$

Also in this case, the Gaussian limit is recovered for $\alpha \to 1$. Conversely, in the limit for $\alpha \to 0$ the kurtosis attains its minimum value $\kappa_{\min}$, where

$$\kappa_{\min} = \begin{cases} \frac{3}{2} & d = 2 \\ \frac{9}{5} & d = 3 \end{cases}. \tag{76}$$

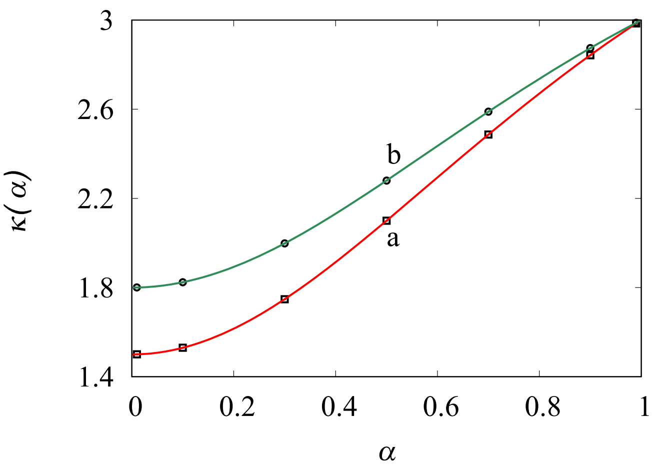

FIG. 5. Kurtosis $\kappa(\alpha)$ vs α. Symbols are the results of stochastic simulations, lines represent the analytical expressions Eqs. (70) and (75). Line a and ○: 2D case; line b and □: 3D case.

Figure 5 depicts the simulation results for the kurtosis compared with the analytical predictions (70) and (75). These results refer to an ensemble of 10^9 realizations of the process.

The density functions for a generic entry of the velocity field (say, v_1 in the 2D case and v_3 in the 3D case) are depicted is Figs. 6 and 7 for the 2D and the 3D case, respectively. The velocities appearing in these figures are normalized to unit variance.

As expected from the analysis of the kurtosis, for low values of α, these distributions deviate significantly from the normal distribution $p_n(v)$,

$$p_n(v) = \frac{1}{\sqrt{2\,\pi}}\, e^{-v^2/2}. \tag{77}$$

In the limit for $\alpha \to 1$, $p^*(v)$ approaches $p_n(v)$ as expected. Already at $\alpha = 0.99$ the resulting normalized velocity density is indistinguishable from the normal distribution.

Deviations from Gaussian velocity distributions have been experimentally observed for cold matter [35–39], and the present model for radiative interactions provides a simple theoretical interpretation of it. In point of fact, the most important conceptual result of the present analysis is that the occurrence of Gaussian velocity distribution at equilibrium is not a "law of nature" but rather the consequence of the range of temperatures at which most of the experiments are performed. Indeed, the values at which $\alpha < 0.9$ in atomic and molecular systems corresponds to very low temperatures ($T < 10^{-6}$ K), and for this reason the prominent field of application of the present analysis involves cold-matter physics.

The equilibrium distributions $f^*(|\mathbf{v}|)$ for the modulus of the normalized velocity $|\mathbf{v}|$ are depicted in Fig. 8 for the sake of completeness, although they do not add any further physical insight to the above analysis of velocity statistics.

As regards the two asymptotic distributions obtained in the limit for $\alpha \to 1$ and $\alpha \to 0$, their mathematical justification is straightforward, but their physical interpretation is rather interesting.

As discussed above, the Gaussian profile is recovered in the limit for $\alpha \to 1$. In the present case, this corresponds to the situation in which the velocity dynamics possesses the

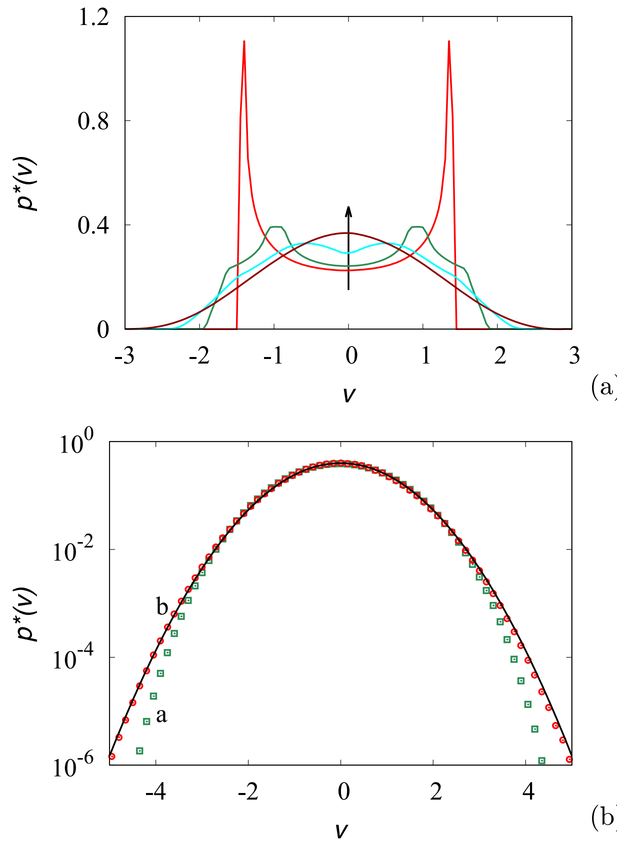

FIG. 6. Equilibrium velocity distribution $p^*(v)$ of a generic Cartesian entry of $\mathbf{v}$ in the 2D case. (a) $\alpha = 0.1, 0.3, 0.5, 0.7$. The arrow indicates increasing values of α. (b) High values of α: symbols (□) correspond to stochastic simulations at $\alpha = 0.9$, symbols (○) at $\alpha = 0.99$. The solid line represents the normal distribution $p_n(v)$.

strongest memory of its past history. The latter interpretation follows also from the exponential decay of the velocity autocorrelation function that, for $\alpha \to 1$, is characterized by an exponent $\eta_r/m \to 0$. In this sense the fluctuation-dissipation relation can be viewed as a dissipation-memory condition for particle-photon interactions (momentum exchange).

In the particle-photon dynamics described by Eq. (36) the above mentioned memory effects (that should not be confused with the lack of Markovianity, as the process is strictly Markovian, and its transition mechanism has no memory) determine the occurrence of a normal distribution for the velocity entries. This phenomenon can be easily interpreted by considering the simplest linear relaxation dynamics for an observable $y(t)$,

$$\frac{dy(t)}{dt} = -\ell\, y(t) - f(t), \tag{78}$$

where $f(t)$ is a stochastic impulsive forcing and $\ell > 0$ the relaxation rate, the solution of which, neglecting the decaying initial condition, is expressed by the convolutional integral

$$y(t) = \int_0^t e^{-\ell(t-\tau)}\, f(\tau)\, d\tau. \tag{79}$$

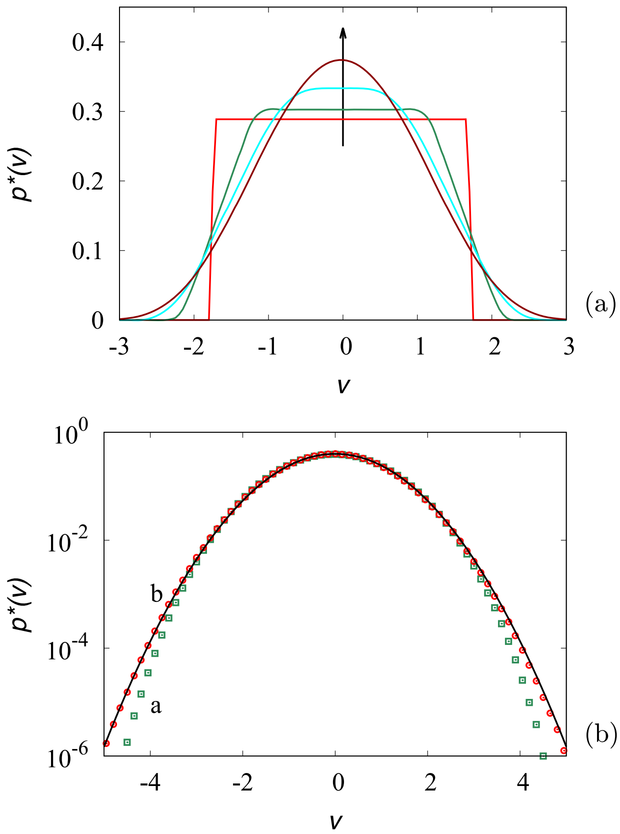

FIG. 7. Equilibrium velocity distribution $p^*(v)$ of a generic Cartesian entry of $\mathbf{v}$ in the 3D case. (a) $\alpha = 0.1,\ 0.3,\ 0.5,\ 0.7$. The arrow indicates increasing values of α. (b) high values of α: symbols (□) correspond to stochastic simulations at $\alpha = 0.9$, symbols (○) at $\alpha = 0.99$. The solid line represents the normal distribution $p_n(v)$.

Assuming $f(t) = \sum_{i=1}^{\infty} f_i\, \delta(t - t_i^*)$, where $t_i^* < t_{i+1}^*$, and f_i generic random variables, we have in the limit for $\ell \to 0$ that

$$y(t) = \sum_{i=1}^{n(t)} f_i, \tag{80}$$

where $n(t)$ is the integer $n(t) = \sum_{i=1}^{\infty} \int_0^t \delta(\tau - t_i^*)\, d\tau$.

Equation (79) clearly indicates that the only physical way for the velocity dynamics could perform a summation of the random photon momentum kicks, corresponding to the classical setting of the CLT, is to possess an infinite memory of its past history, corresponding to $\ell \to 0$. In this case, the velocity dynamics corresponds to the summation of the independent random kicks induced by the photon bath.

It is also interesting to consider the other limit, $\alpha \to 0$, corresponding to the complete absence of memory in velocity dynamics, as Eq. (44) reduces in this limit to

$$\mathbf{v}_{n+1} = \beta\, \mathbf{r}_{n+1}, \tag{81}$$

and consequently, the velocity statistics is simply a rescaled sampling of the statistics of photon momenta. Consider the 2D case, and let v a velocity entry, say, v_1, for which in the limit for $\alpha \to 0$ we have (upon normalization)

$$v = \sqrt{2}\, \cos\phi, \tag{82}$$

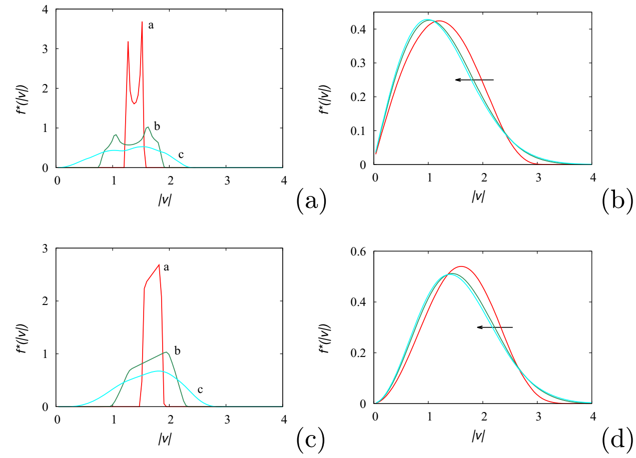

FIG. 8. Equilibrium distributions $f^*(|\mathbf{v}|)$ of the modulus $|\mathbf{v}|$ obtained from stochastic simulations. (a, b) 2D case; (c, d) 3D case. Lines a refer to $\alpha = 0.1$; lines b to $\alpha = 0.3$; lines c to $\alpha = 0.5$. The arrows in panels (b) and (d) indicate increasing values of $\alpha = 0.7,\ 0.9,\ 0.99$.

ϕ being uniformly distributed in $[0, 2\pi)$. The equilibrium distribution function for v is thus given by

$$F^*(v) = \frac{1}{2\pi} \int_{\{\sqrt{2}\cos\phi < v\}} d\phi = \frac{1}{\pi} \int_{\arccos y/\sqrt{2}}^{\pi} d\phi$$
$$= = 1 - \frac{1}{\pi} \arccos\left(\frac{v}{\sqrt{2}}\right) \tag{83}$$

in the interval $v \in (-\sqrt{2}, \sqrt{2})$, while $F^*(v) = 0$ for $v < -\sqrt{2}$ and $F^*(v) = 1$ for $v > \sqrt{2}$. Differentiating $F_v^*(v)$ with respect to v, the density function $p^*(v)$ follows

$$p^*(v) = \frac{1}{\sqrt{2}\,\pi} \frac{1}{\sqrt{1 - v^2/2}}, \qquad v \in (-\sqrt{2}, \sqrt{2}) \tag{84}$$

and zero otherwise. Figure 9(a) compares the results of stochastic simulations of the velocity dynamics via Eq. (44) at low α values, and the analytical expression for the limit velocity density function (84) in the 2D case. Analogously, in the 3D case, by considering $v = v_3 = \sqrt{3}\cos\theta$, $\theta \in [0, \pi)$, we have

$$F^*(v) = \frac{1}{2} \int_{\arccos(v/\sqrt{3})}^{\pi} \sin\theta\, d\theta = \frac{1}{2}\left(1 + \frac{v}{\sqrt{3}}\right) \tag{85}$$

in $v \in (-\sqrt{3}, \sqrt{3})$. Consequently, the density function $p^*(v)$ is piecewise constant in the limit for $\alpha \to 0$,

$$p^*(v) = \begin{cases} \frac{1}{2\sqrt{3}} & v \in (-\sqrt{3}, \sqrt{3}) \\ 0 & \text{otherwise} \end{cases}, \tag{86}$$

as depicted in Fig. 9(b).

This result is interesting from another point of view. The case $\alpha \to 0$, corresponds physically to $\gamma \to \infty$, i.e., to the low-temperature limit. In these conditions, the statistics of particle velocity corresponds to the pure sampling of the randomness in the orientation of the incoming photons. Due to isotropy, these orientations are distributed uniformly on the surface of the unit sphere. As can be observed from Fig. 9 and from the calculations in the main text, the shape of the

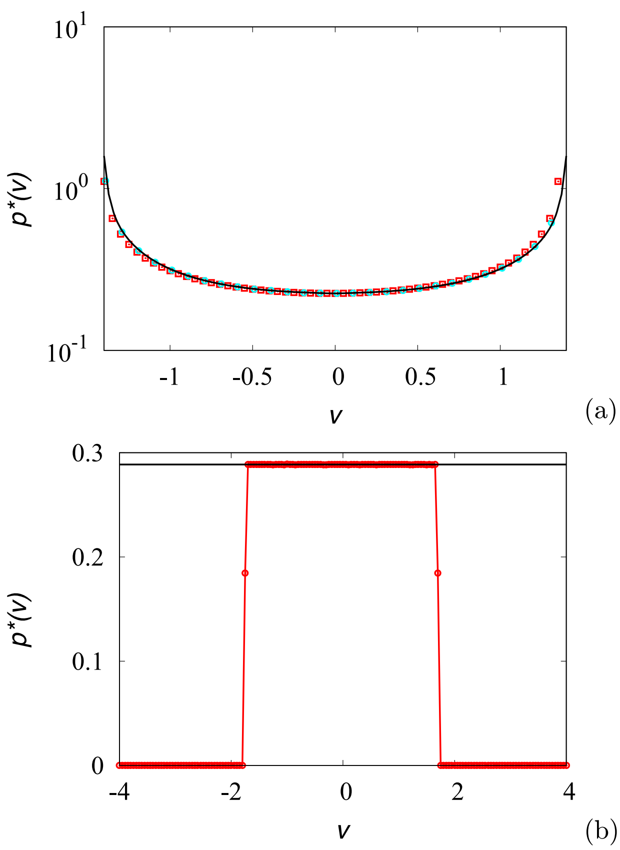

FIG. 9. Equilibrium velocity distribution $p^*(v)$ at low α values. (a) 2D case. Symbols represent the results of stochastic simulations at $\alpha = 0.01$ (□) and $\alpha = 10^{-6}$ (○). The solid line is the analytical expression Eq. (84). (b) 3D case. Symbols represent the results of stochastic simulations at $\alpha = 0.01$. The horizontal line is the analytical value $p^*(v) = 1/2\sqrt{3}$.

equilibrium distributions $p^*(v)$ strongly depends qualitatively on the dimension of the physical space in which photons travel. Therefore, it is conceptually possible to obtain the experimental determination of the dimension d, $d = 2, 3, \ldots$, of the physical space from measurements of $p^*(v)$.

VII. CONCLUDING REMARKS

This article has focused on radiative processes and their thermalization properties in molecular systems (gases), neglecting the influence of particle-particle collisions. This restriction is aimed at isolating the role of emission and absorption processes for understanding their peculiar features. The interplay between radiative processes and elastic collisions will be addressed in a forthcoming work, merging the theory developed in this article with the formalism developed in [16,17]. Whenever the frequency of particle-particle collisions is much less than that of radiative events, the velocity density function is controlled by the latter. This means that in this case, physically corresponding to highly rarefied conditions and very low temperatures, deviations from Gaussianity can be expected. Under these conditions, i.e., when the thermalization process is controlled by radiative processes, the equation for the temporal evolution of particle momentum can be expressed in the form of a nonlinear impulsive differential equation, driven by the distributional derivative of a Poisson counting process. This formulation, which accounts for the Einstein representation of radiative processes, introduces the concept of a radiative mass η, describing statistically the dissipative recoil effect associated with a radiative transition between two energy levels. At high temperatures, the radiative mass is smaller than the inertial mass, while it diverges for $T \to 0$. From this formulation, a radiative fluctuation-dissipation theorem can be derived, associated with the exponential decay of the velocity autocorrelation function.

The velocity distribution function has been thoroughly analyzed. In the limit of small radiative friction, the velocity distribution converges to the Maxwellian (Gaussian) profile, while in the limit of high radiative dissipation it converges to Eq. (83) controlled by the random and uniform distribution of the incoming and emitted photons. Deviations from Gaussianity are not surprising, as the momentum equation (36) bears some similarity with the approach followed in [40] for the statistical mechanical properties of a thermal system. For the sake of completeness, it should be observed that, while the values of $\langle v_i^2 \rangle$ are not affected by elastic particle-particle collisions, the latter modify significantly the shape of the velocity distribution function. Experiments on cold atoms have already shown deviations from Gaussian velocity distributions [35–39], and this represents a qualitative support to the theory developed in this article. Further experimental work at very low temperatures, using, e.g., laser cooling techniques, may provide a quantitative confirmation of the present analysis, or the necessity of its generalization and extension.

APPENDIX: NONLINEAR IMPULSIVE DIFFERENTIAL EQUATIONS

The analysis of differential equations of the form (36) and (37), in which the impulsive forcing is modulated by a function of the unknown variable (a situation that can be referred to as a nonlinear impulsive differential equation, in analogy with the definition of nonlinear Langevin equations) poses mathematical problems similar to those encountered for the nonlinear Langevin equations (driven by a Wiener forcing), associated with the Itô-Stratonovich dilemma. The mathematical problems arise because the function $\mathbf{v}(t)$ is discontinuous at $t = t^*$, and, therefore, a rule should be specified to interpret this equation. In most of the literature [24–26] a midpoint rule as been adopted. Let $\mathbf{v} = \mathbf{v}(t_-^*)$ and $\mathbf{v}' = \mathbf{v}(t_+^*)$, where $t_\pm^* = \lim_{\varepsilon \to 0} \mathbf{v}(t^* \pm \varepsilon)$, $\varepsilon > 0$, and integrate Eq. (37) in the interval $[t^* - \varepsilon, t^* + \varepsilon]$ taking the limit for $\varepsilon \to 0$,

$$m\,(\mathbf{v}' - \mathbf{v}) = \int_{t_-^*}^{t_+^*} [-\eta\,\mathbf{v}(t) + \mathbf{b}]\,\delta(t - t^*)\,dt, \qquad \text{(A1)}$$

and the midpoint rule assumes that for the integral containing $\mathbf{v}$

$$\int_{t_-^*}^{t_+^*} \mathbf{v}(t)\,\delta(t - t^*)\,dt = \frac{\mathbf{v}' + \mathbf{v}}{2}, \qquad \text{(A2)}$$

so that Eq. (A1) becomes

$$m\,(\mathbf{v}'-\mathbf{v}) = -\eta\left(\frac{\mathbf{v}'+\mathbf{v}}{2}\right) + \mathbf{b}. \tag{A3}$$

This approach has been critically confuted in [27] on the basis of simple principles of calculus. In point of fact, expressing Eq. (37) componentwise,

$$m\,\frac{dv_i}{\eta\,v_i - b_i} = -\delta(t-t^*)\,dt, \tag{A4}$$

$i = 1, 2, 3$, integrating over (t_-^*, t_+^*),

$$\frac{m}{\eta}\int_{t_-^*}^{t_+^*}\frac{dv_i}{v_i - b_i/\eta} = -\int_{t_-^*}^{t_+^*}\delta(t-t^*)\,dt, \tag{A5}$$

one finally obtains

$$\frac{m}{\eta}\,\log\left(\frac{v_i' - b_i/\eta}{v_i - b_i/\eta}\right) = -1, \tag{A6}$$

leading to Eq. (38). In the limit for $\eta/m \ll 1$, the midpoint rule is recovered.

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