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The generalized Langevin equation revisited: Analytical expressions for the persistence dynamics of a viscous fluid under a time dependent external force

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HIGHLIGHTS

- The generalized Langevin equation is solved analytically for a viscoelastic fluid.
- Alternative stochastic equations are derived for a diffusing dense fluid particle.
- The Fluctuation–Dissipation theorem is generalized for a fluid in an external field.
- A self-contained definition of diffusion coefficient is provided.
- The short time dynamics within absorbing boundaries fits the MD simulations.

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ABSTRACT

The non-static generalized Langevin equation and its corresponding Fokker–Planck equation for the position of a viscous fluid particle were solved in closed form for a time dependent external force. Its solution for a constant external force was obtained analytically. The non-Markovian stochastic differential equation, associated to the dynamics of the position under a colored noise, was then applied to the description of the dynamics and persistence time of particles constrained within absorbing barriers. Comparisons with molecular dynamics were very satisfactory.

1. Introduction

The dynamics of particles in a potential field is usually investigated by molecular dynamics (MD). However, since the time scale of such a procedure is of the order of femtoseconds, the algorithms are in general very expensive in computer consuming time. To overcome this difficulty, one generally appeals to mesoscopic descriptions on which the time scale is larger. It gives a glimpse about the dynamical behavior of the system at the time scale of the technique. There are three levels of description. The most commonly used description is the so called Langevin equation (LE), where the dynamics of a Brownian particle in phase space is described by the Markovian set of stochastic differential equations (SDE) [1–3]

$$\begin{aligned} m\frac{\mathrm{d}\,v(z,t)}{\mathrm{d}t} &= -\gamma(z)\,v(z,t) + \eta(z)\,\xi(t) + F(z,t), \\ \dot{z} &= v, \end{aligned} \tag{1}$$

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where $z(t)$ and $v(z,t)$ are the position and velocity of the tagged particle of mass m at time t, respectively; $\gamma(z)$ is the position-dependent phenomenological fluid friction coefficient; $F(z,t)$ is the external force field, $\eta(z)$ is the intensity of the stochastic force and $\xi(t)$ is a zero-mean Gaussian white noise term. The static LE can be solved by a double integration or alternatively, through the solution of a second order differential equation [1,3]. In fact, an analytical solution for a confined fluid has been previously given [4].

An important simplification of the LE with a wide range of practical applications is the so-called Smoluchowski limit also known as the high friction limit (HFL). The most simple derivation consists on assuming that the fluid has a large enough friction coefficient γ so that the velocity in the LE shows a fast relaxation to a quasi equilibrium [5], with $dv/dt = 0$. Thus, position evolves with time according to

$$\frac{dz}{dt} = v_F(z) + \sqrt{2D_0}\,\xi(t), \tag{2}$$

where $v_F(z) = F(z,t)/\gamma(z)$ is the induced velocity drift and $D_0 = (1/2)(\eta(z)/\gamma(z))^2$ is interpreted as a diffusion coefficient. The corresponding master equation for the probability density corresponding to this SDE is the Smoluchowski equation (SE). Clearly this is only valid in the long time limit, also known as the Smoluchowski regime. The third stochastic description is an improvement without restriction on the time scale, known as the non-static or *generalized Langevin equation (GLE)*. It is obtained modifying the dissipation or friction term

$$m\frac{d\,v(z,t)}{dt} = -m\int_0^t \Gamma(z,t-t')\,v(z,t')\,dt' + R(t) + F(z,t), \tag{3}$$

where the kernel $\Gamma(z,t-t')$ expresses the memory or retardation effect on the movement of the fluid particle due to the collective hydrodynamic response of the surrounding fluid [6] and, $R(t) = \eta(z,t)J(t)$ a colored-Gaussian fluctuating driving force. Now the random noise function $J(t)$ is not a white noise. If the retardation is omitted, the kernel is static $\Gamma(z,t-t') = \alpha(z)\,\delta(t-t')$ with $\alpha(z) = \gamma(z)/m$, and the LE, Eq. (1), is recovered. This is equivalent to take the noise as being white, namely, $J(t) = \xi(t)$. However, when inertial effects are not negligible – the friction coefficient is not dominant in the dynamics – the position and velocity are driven by non-Markovian random terms having a finite correlation time. This is the situation for real non homogeneous fluids and systems with strong boundary conditions or in the presence of chemical reactions.

A well known work obtaining a master equation for the probability density $p(\zeta,t \mid \zeta_0)$ for a general ζ process, as a Kramers–Moyal [7] cumulant expansion, is due to Hänggi in 1978 [8,9]. However, the GLE, Eq. (3), was discussed for a viscous fluid by Chow and Hermans [10] as far back as 1972 and a master equation for that generalized version, was nicely derived and solved by Dufty [11] in 1974, being commonly referred to as the Fokker–Planck equation. In the absence of external forces it was extensively studied by Adelman [12], Fox [13], Volkov and Pokrovsky [14] and later by Rodríguez–Salinas [15]. Numerical approaches for general first-order SDEs with colored random forces have been also presented [16,17]. Budini and Cáceres [16], numerically obtained the velocity distribution associated to the GLE SDE for arbitrary noise and memory kernels, but with no external force. They found that the interplay of noise structure and dissipation is an important issue to consider, in order to achieve the stationary steady state of the probability density.

In this paper we analyze the dynamical or generalized Langevin approach, Eq. (3), for the motion of an interacting fluid particle in an external time-dependent field. We obtain the corresponding generalized Fokker–Planck equations (GFPE) for the Bayesian probabilities $p(v,t|v_0,0)$ and $p(z,t|z_0,v_0,0)$. Then, following Chandrasekhar's approach [18], we obtain the v_0 averaged probability densities $p(v,t)$ and $p(z,t|z_0,0)$ giving analytical formulas for their moments. We shall discuss the fact that this equation can be written as a much simpler statistically equivalent Markovian first-order SDE. Revisiting the master equation associated to GLE, we get consistent analytical results for the survival probability in a viscous fluid and evaluate important dynamical properties as the mean square displacement (MSD) for a fluid bounded by absorbing barriers.

Analytical expressions for Chandrasekhar conditional probability density $p(z,t|z_0,v_0)$ and the corresponding Rayleigh type GFPE in the presence of an external force are presented in Section 2. That is, with the method based on the solution of the stochastic Liouville equation [19–21], we find a well defined GRFPE, whose analytical solution matches Chandrasekhar's lemma [18].

Section 3 deals with the GLE's velocity and position space distribution moments for any given external time dependent force $F(t)$. First, we revise the GLE z-space to find the moments of the probability density $p(z,t|z_0)$ averaged over the initial velocity, unifying all the equivalent master equations and SDE. The known results on the velocity space probability [12,13] are complemented to include a time dependent external force.

Considering an exponential decaying friction coefficient kernel and an external constant force, we derive in Section 4, analytical results for the moments of the distributions in z and v spaces. The application of the GLE theory to the problem of survival probability and first passage time of a constrained fluid is presented in Section 5.

Finally, we include two appendices to show an unified view of the velocity-fluctuation coefficient in the GLE approach and the classical LE and SE results.

2. The position generalized Rayleigh–Fokker–Planck equation (z-GRFPE)

In this section, we use the simple procedures well discussed by Adelman [12], Fox [13] and Sancho et al. [21], to obtain the GFPE type master equations associated to the position of the particles of a viscous fluid satisfying the GLE. It has been