



Fractional correlation functions in simple viscoelastic liquids



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HIGHLIGHTS

- Fractional derivatives are incorporated into fluctuating transport equations of a viscoelastic liquid.
- Fractional fluctuations enhance the longitudinal velocity autocorrelation.
- Fractional fluctuations decrease the light scattering spectrum and the intermediate scattering function until a crossover is reached.

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ABSTRACT

We develop a hydrodynamic formulation of fractional fluctuations in a viscoelastic liquid whose longitudinal modulus is a scalar and only depends on time. The method is based on the introduction of fractional time derivatives in the hydrodynamic equations due to the viscoelastic memory. Coupled generalized Langevin equations for the fluctuations of the state variables are formulated and solved analytically for a power-law memory kernel with long correlation noise. The associated fractional Fokker–Planck equation (FFPE) is also derived and it is shown that it exhibits a fluctuation–dissipation theorem (FDT). The explicit analytic diffusion coefficient is calculated for power law viscoelasticity and is shown to be subdiffusive. The fractional correlations for longitudinal velocity and density fluctuations are analytically calculated and used to obtain the light scattering spectrum and the intermediate scattering function of the viscoelastic fluid. Our model calculation predicts that the fractional effects on these properties are not small effects and might be measurable.

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1. Introduction

In a dynamic system where the central limit theorem (CLT) applies, there exists a well-defined separation between the time scales associated with the macroscopic transport processes and the microscopic ones giving rise to them. This separation enables a smoothing process over the microscopic degrees of freedom resulting in stochastic differential equations of motion over macroscopic time scales, which can be formulated and solved with the methods of ordinary calculus in terms of ordinary derivatives. On the other hand, when this separation of time scales does not exist, the smoothing process is no longer feasible and the usual formalism based on ordinary calculus is no longer adequate to describe the transport processes [1]. Then the transport equations cannot be expressed in terms of ordinary differential calculus and this forces the time derivative in the transport equations to be replaced by a fractional time derivative. In this way fractional stochastic differential equations on the mesoscopic level replace the conventional Langevin equation description [2–4]. Examples of this situation

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are the large variety of relaxation processes that occur in complex systems like viscoelastic fluids, glassy materials, synthetic polymers or biopolymers, all of which have in common that their relaxation functions are non-exponential, due to the large number of highly coupled elementary units responsible for the relaxation. As a consequence, the *CLT* may not be applicable and the requirement of high cooperation between these elements leads to slower decays often modeled by empirical power-laws [5,6].

Although fractional Brownian motion (*FBM*) has been extensively used as a prototype system in the modeling of anomalous diffusion and has given rise to a huge literature [7,8], much less is known of the implications of fractional effects on hydrodynamic systems [9–11]. In the fractional stochastic formalism used in this work, we still follow the traditional way of describing viscoelastic effects through memory kernels in the transport equations. However, we model them by a power-law, which introduces long-time range effects that may mix macroscopic and microscopic time scales. As a result, the fluctuations exhibit a *strange dynamics* and there is no preferred time scale [8]. One way of taking this feature into account in the dynamics, is by replacing the normal time derivative in the transport equations by a fractional one to get a consistent description [12].

As will be seen in this paper, the non-existence of separation of time scales also occurs in the description of the dynamics of fluctuations of a viscoelastic liquid. We will show that the description of hydrodynamic fluctuations in these systems may be formulated in terms of generalized fractional Langevin equations with time-dependent memory kernels for the time evolution of the hydrodynamic fluctuations [13]. The motivation for studying these fluids is to consider physical systems and measurable properties that are different from those who are usually calculated in *FBM*, random walks and anomalous diffusion, and that allow to estimate quantitatively the effect of fractional derivatives. To our knowledge, the study of these effects on fluid properties has been scarcely considered in the literature.

More specifically, our main purpose here is to investigate the effect produced by fractional fluctuations on the dynamics of two equilibrium correlation functions of a viscoelastic liquid, namely, its longitudinal velocity and density fluctuations correlations. The latter correlation is related to some light scattering properties like its dynamic structure factor, $S(\vec{q}, \omega)$, and its intermediate scattering function, $F(\vec{q}, t)$, as functions of the wavevector $\vec{q}$, frequency ω or time t . To this end we introduce a simple hydrodynamic model for the translational motion of a viscoelastic liquid with (spatially) homogeneous viscoelastic properties. Caputo's fractional time derivatives [14], and random forces are incorporated into the transport equations, which are thus converted into linear generalized fractional Langevin equations describing the dynamics of the fluctuations of the hydrodynamic state variables. Using known analytic results available in the literature, we solve these equations and quantify the effect of fractional fluctuations on the longitudinal velocity and the density correlation functions.

To this end this work is organized as follows. In Section 2 we introduce a model describing only the translational degrees of freedom of a viscoelastic liquid. The model is simple enough for easy, explicit mathematical manipulation and allows us to obtain explicit analytic results, but it is also realistic enough to capture the essential features of a viscoelastic liquid. We first set up the basic linearized hydrodynamic equations for the fluctuations of its state variables when the system is close to equilibrium. Then, in Section 3 we introduce the Caputo fractional time derivative and derive a complete set of fractional hydrodynamic equations with memory for the fluctuations of the local mass density, longitudinal and transverse velocity fluctuations of the system in the linear response regime. In the next Section 4 we introduce additive and Gaussian stochastic forces with long-range correlation, to obtain a coupled set of fractional generalized Langevin equations (*FGLE*). We also derive the associated *FFPE* and show that it has a general structure that complies with the physical restrictions of linear response and, using known results from the literature, we discuss how this guarantees the existence of a *FDT*. Moreover, the diffusion coefficient in this equation can be explicitly calculated for power-law viscoelasticity and we show that the diffusion process associated with this *FFPE* is subdiffusive. From the *FGLE*'s we then obtain analytic expressions for the fractional correlation function of the longitudinal velocity fluctuations, $\hat{C}_{v_z}^f(q, t)$. This fractional quantity is evaluated in the limit of long times for Salol, a glass forming liquid obeying a power-law rheological equation of state, and we compare its behavior with the usual thermal (non-fractional) corresponding correlation. We find that for derivatives of fractional order α in the interval $0 < \alpha < 1$, there may be a significant large relative change between these correlations. In particular, the ratio, $R(t; \alpha, \lambda)$, of the fractional to the non-fractional correlation, parameterized by the degree of viscoelasticity (λ) and $\alpha \sim 0.9$, shows a large relative change corresponding to an increase of up to *two orders of magnitude* due to the presence of fractional fluctuations. In Section 5 we calculate the density fluctuations correlation function, $\hat{C}_\rho^f(q, s)$, and calculate the corresponding fractional dynamic structure factor, $\tilde{S}^f(q, \omega)$, by taking its real part. In this case the ratio $P(q, t; \alpha, \lambda)$ of the fractional to the non-fractional spectra for frequencies and wave-numbers typical of a light scattering experiment, shows a different behavior than $R(t; \alpha, \lambda)$. In this case we find that the fractional spectrum is smaller than the non-fractional one, but it may reach up to a 77% value of the non-fractional one. This is not a small effect and might be measurable. Also, in Section 5 we use a novel analytic procedure to calculate the inverse Laplace transform of $\hat{C}_\rho^f(q, s)$ to obtain the fractional intermediate scattering function (*FISF*) $F^f(q, t)$. We find that the behavior of *FISF* as a function of time is similar to the one found for the fractional spectrum $\tilde{S}^f(q, \omega)$, namely, the corresponding ratio $Q(t; \alpha, \lambda)$, shows that the fractional $F^f(q, t)$ is smaller than the non-fractional one. For the time interval considered, Q may be $\sim 67\%$ of the non-fractional one. Again, the size of the relative changes in $\tilde{S}^f(q, \omega)$ and $F^f(q, t)$ suggest that these fractional effects might be measurable; however, we are not aware of any experimental results to compare with and it is not possible to conclude from our analysis if these enhancements of some properties are measurable. This is an open issue that remains to be assessed. Finally, in Section 6 we summarize the main results of our work and make some further physical remarks.

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