Rheology modulated non-equilibrium fluctuations in time-dependent diffusion processes

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HIGHLIGHTS

- The auto-correlation function (static and dynamic structure factor) of concentration fluctuations is determined for viscoelastic fluids.
- The transverse component of velocity fluctuations which influences Rayleigh spectrum is obtained for viscoelastic fluids.
- Criteria for the appearance of peaks at non-zero frequency for the case of dynamic structure factor is obtained for viscoelastic fluids.
- Contrary to the equilibrium scenario the non-equilibrium Rayleigh line is influenced by viscoelastic effects.

ARTICLE INFO

ABSTRACT

The effect of non-Newtonian rheology, manifested through a viscoelastic linearized Maxwell model, on the time-dependent non-equilibrium concentration fluctuations due to free diffusion as well as thermal diffusion of a species is analyzed theoretically. Contrary to the belief that non-equilibrium Rayleigh line is not influenced by viscoelastic effects, through rigorous calculations, we put forward the fact that viscoelastic effects do influence the non-equilibrium Rayleigh line, while the effects are absent for the equilibrium scenario. The non-equilibrium process is quantified through the concentration fluctuation auto-correlation function, also known as the structure factor. The analysis reveals that the effect of rheology is prominent for both the cases of free diffusion and thermal diffusion at long times, where the influence of rheology dictates not only the location of the peaks in concentration dynamic structure factors, but also the magnitudes; such peaks in dynamic structure factors are absent in the case of Newtonian fluid. At smaller times, for the case of free diffusion, presence of time-dependent peak(s) are observed, which are weakly dependent on the influence of rheology, a phenomenon which is absent in the case of thermal diffusion. Different regimes of the frequency dependent overall dynamic structure factor, depending on the interplay of the fluid relaxation time and momentum diffusivity, are evaluated. The static structure factor is not affected to a great extent for the case of free-diffusion and is unaffected for the case of thermal diffusion.

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1. Introduction

A system at a finite temperature exhibits spontaneous and continuous microscopic fluctuations in quantities such as density, pressure, temperature, velocity field etc. about a mean value [1]. The fluctuations are dissipated in the system

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through various processes like diffusion, viscous flow or thermal conduction, much like the way in which external disturbances are relaxed. In course of this relaxation, each mode or degree of freedom of the system tries to return to the original state which can be a state of thermal equilibrium or non-equilibrium (which is assumed to be locally in thermal equilibrium). In the principle of local equilibrium, it is assumed that the macroscopic level can be divided into smaller systems which are infinitesimally smaller as compared to the macroscopic level but still contain sufficiently large number of molecules, so that statistical averages can be performed locally [2]. Notably, the local thermodynamic variables and other associated local thermodynamic properties remain interrelated by the same relations as for a thermodynamic equilibrium state.

Fluctuations in fluids in thermodynamic equilibrium have been studied to a great extent [2]. It is a very well-established fact that the correlation functions associated with the thermal fluctuations of fluid in equilibrium are spatially short ranged [2,3] (except for states near a critical point), unlike the case for fluids which are not in equilibrium. It is also well known that this long-ranged nature is caused by a coupling between hydrodynamic modes through the externally imposed non-equilibrium fluxes or gradients [3,4]. Thermal fluctuations are characterized by space–time functions that account for the correlation between the value of a quantity at some position and time with its value at a different position and time; these can be typically represented as a space–time correlation function $C_{AB}(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2) = V \langle \delta A(\mathbf{x}_1, t_1) \delta B(\mathbf{x}_2, t_2) \rangle$ [1,2] where δA and δB denote the fluctuations in the dynamical variables under consideration, the subscripts denote two different states 1 and 2 respectively and the parameter V denotes a multiplication prefactor. When A and B are the same variables, we obtain the autocorrelation function. When one considers the correlation function of density, one obtains the structure factor/density correlation function. The equal-time or static structure factor is defined as $S(k, 0) = \langle \delta c_{k,0} \delta c_{k,0}^* \rangle$ whereas the dynamic structure factor is defined as $S(k, \omega) = \langle \delta c_{k,\omega} \delta c_{k,\omega}^* \rangle$ [2,5], where asterisk denotes the complex conjugate (via Fourier transform of the quantities). The intensity of the fluctuations is determined by equal-time correlation functions, whereas time-dependent correlation functions are used for determining the dynamical properties of fluctuations [2]. Several researchers have employed light scattering measurements as means to directly observe the evolution of the dynamic structure factor [1,2,6–8]. In these experiments, the wavenumber of observation is that associated with momentum transfer between the light and the sample during scattering which is approximately given by $\lambda = \frac{\lambda_0}{2} \sin(\theta/2)$ [1], where λ is the scattered wavelength, λ_0 is the incoming wavelength of light and θ is the scattering angle (angle formed between the incoming and outgoing beams).

Recent developments in laser technology have led to the usage of He–Ne laser (6.328 pm) to measure the density correlation function for a wide variety of mixtures [1]. Steady state non-equilibrium fluctuations for a non-critical binary mixture in the presence of temperature gradient have been studied [7], where large enhancement to the so called Rayleigh line from concentration fluctuations, depending upon the square of the concentration gradient, has been predicted. Measurement of Soret and mass diffusion coefficients have been studied [9,10] by investigating non-equilibrium concentration fluctuations. Non-equilibrium fluctuations under the influence of gravity also have been studied in Ref. [11]. Fluctuations for isothermal free diffusion cases (the so called the non-Soret flux) have been studied by some researchers [5]. In such a process, the concentration evolves in space and time on a time scale much slower than the time scale of the fluctuations and hence, these processes can be considered to be quasi-stationary for fluctuations [5], while performing the Fourier transform for obtaining the structure factor. Thus, Vailati and Giglio [5] have obtained the static structure factor at any time t by assuming a local equilibrium. For time dependent non-equilibrium diffusive processes, it is observed that the static structure factor shows a dramatic increase as compared to the value at equilibrium. However, for the case of non-equilibrium fluctuations at the steady state, the static structure factor depicts a k^{-4} divergence at large wave numbers (k); these phenomena were also observed in experimental findings in the non-equilibrium fluctuations of binary mixture of aniline and cyclohexane [5]. Some experiments and theoretical works have showed the presence of unexpectedly large fluctuations in free diffusion processes [12–14], which can be attributed to the coupling between the concentration and velocity fluctuations in non-equilibrium state [13].

While it is typical to consider an unbounded fluid domain for calculations, the importance of bounding length scales has been discussed in many works which deal with the finite sized effects for fluids or fluid mixtures bounded by boundaries [15–19]. The asymptotic behavior for certain range of dimensionless wave-numbers truly highlights the importance of accounting for the boundedness of the problem, which is manifested in the form of an intermediate length scale that affects the diffusion process. Through similar argument, in the case of non-Newtonian fluids, it is imperative to include the intermediate relaxation time scale of the fluid. This time scale is larger than the molecular relaxation time scale. Regardless, we expect that the relaxation time will play an important role towards dictating the structure factor at some time scale or the other. Some studies for equilibrium or non-equilibrium stationary states of complex fluids have been carried out [20,21]. Small-angle Rayleigh light-scattering measurements in polymer solutions under external temperature gradients have been performed and it has been reported that the concentration fluctuations are enhanced and are proportional to $(\nabla T)^2/k^4$, where k is the wavenumber and ∇T is the external temperature gradient [22].

By theoretically considering the solution of Maxwell fluids, de Haro et al. have demonstrated [23] that although the Mountain peak [24–26] is undisturbed by the viscoelastic nature of the fluid, the Brillouin peak (velocity correlations) becomes narrower and the asymmetry between the two Brillouin peaks increases [23]. On a separate note, the dynamic structure factor for a suspension of particles in a viscoelastic medium depicts alterations in the magnitude owing to the time-memory effects due to the relaxation time of the Maxwell fluid [27]. The presence of multiple relaxation time scales also leads to an enhancement in the concentration fluctuations; a notion which is associated with the so called resonance