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Stochastic characteristics and Second Law violations of atomic fluids in Couette flow

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HIGHLIGHTS

- An equation relating density contrast to shear stress fluctuations is proposed.
- Violations of the 2nd law of thermodynamics is observed via the shear stress.
- Identify primary variables of interest as density contrast and shear stress.
- variables affect flow stability leading to shear-thinning at critical strain rate.
- Changes in statistical nature of the variables help identify critical strain rate.

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ABSTRACT

Using Non-equilibrium Molecular Dynamics (NEMD) simulations, we study the statistical properties of an atomic fluid undergoing planar Couette flow, in which particles interact via a Lennard-Jones potential. We draw a connection between local density contrast and temporal fluctuations in the shear stress, which arise naturally through the equivalence between the dissipation function and entropy production according to the fluctuation theorem. We focus on the shear stress and the spatio-temporal density fluctuations and study the autocorrelations and spectral densities of the shear stress. The bispectral density of the shear stress is used to measure the degree of departure from a Gaussian model and the degree of nonlinearity induced in the system owing to the applied strain rate. More evidence is provided by the probability density function of the shear stress. We use the Information Theory to account for the departure from Gaussian statistics and to develop a more general probability distribution function that captures this broad range of effects. By accounting for negative shear stress increments, we show how this distribution preserves the violations of the Second Law of Thermodynamics observed in planar Couette flow of atomic fluids, and also how it captures the non-Gaussian nature of the system by allowing for non-zero higher moments. We also demonstrate how the temperature affects the band-width of the shear-stress and how the density affects its Power Spectral Density, thus determining the conditions under which the shear-stress acts is a narrow-band or wide-band random process. We show that changes in the statistical characteristics of the parameters of interest occur at a critical strain rate at which an ordering transition occurs in the fluid causing shear thinning and affecting its stability. A critical strain rate of this kind is also predicted by the Loose–Hess stability criterion.

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1. Introduction

With the recent proliferation of MEMS and NEMS systems, understanding fluid dynamics at the microscale and nanoscale is becoming crucial to facilitating continuous development in this area. When the system size is small, i.e. in the micro or nanoscale, classical models based on continuum theories are insufficient. Such systems require a statistical treatment rather than a deterministic one. To characterize the statistical nature of such systems, one needs to resort to Molecular Dynamics (MD) simulation techniques in order to extract pertinent information regarding the statistical moments and the temporal and spectral characteristics.

The NEMD techniques and, in particular, the SLLOD equations of motion, are well established and documented tools to model atomic fluids undergoing planar Couette flow [1–3]. Owing to the chaotic nature of molecular movement and interactions within the flow field, the state variables of interest are accompanied by significant fluctuations, and thus must be dealt with in a statistical sense. In the specific case of a planar Couette flow, we focus on the statistics of the shear stress and density fluctuations.

Molecular and atomic flows often display exotic and peculiar characteristics. For instance, it has been widely observed in NEMD simulations that fluids display extreme shear-thinning behavior as displayed by the dramatic change in slope of the stress-deformation curve and the change in viscosity with shear rate [4–7]. Such non-Newtonian behavior is quite surprising considering the fluid is homogeneous and isotropic, to begin with. In fact, the anisotropy usually associated with shear thinning is induced in the fluid at sufficiently large strain rates as the molecules tend to realign themselves into string-like structures [8–11]. This leads to a dramatic drop in shear stress between fluid layers, subsequently resulting in a drop in viscosity. As another example of exotic behavior, from a thermodynamic perspective, such systems have been observed to violate the Second Law of thermodynamics, which only holds true in the long-time limit, or large volume limit, or in a statistically average sense [12,13]. In contradistinction to deterministic continuum mechanics, in sub-continuum systems, owing to the probabilistic nature of the shear stress, there is a finite probability of negative shear stress increments which signifies negative entropy production. For these reasons, it is useful to understand and capture the temporal and structural mechanisms that lead to this observed behavior. Such models would be useful as inputs for more advanced fluid dynamics simulations.

Shear thinning and the associated ordering in the flow direction have important consequences for flow stability. It was shown by Loose and Hess (Ref. [14]) and by McWhirter (Ref. [15]) that this is the nonlinear regime in which stable flow of an amorphous fluid is no longer possible. The stability criterion explicitly uses the shear stress and normal stresses to detect the critical strain rate at which flow instability sets in. This phenomenon was demonstrated to be a consequence of the thermostatting mechanism in the SLLOD equations of motion, which describe the microscopic Couette flow [10]. It manifests itself as a dramatic change in the slope of the stress-deformation plot [7], and can lead to subcritical transitions and flow instability [16,17].

In this article, we use NEMD with the SLLOD equations to study the statistical and structural features of atomic fluids that undergo Couette flow, with the particles interacting via a Lennard-Jones (LJ) potential. In particular, we study the autocorrelation function, power-spectral density, and bi-spectrum of the shear stress and local density fluctuations to gain insight into the shear-thinning characteristics of this system and its departure from a Gaussian system. We motivate the need to study these variables by illustrating the natural connection between them as a consequence of the fluctuation theorem. Using principles of information theory, we derive a probabilistic model for the shear stress that accounts for negative shear stress increments and thus for violations of the Second Law of thermodynamics. We describe the departure from Gaussian statistics as the fluid enters the nonlinear flow regime and describe how these changes can be used to identify the critical strain rate, and thus justifying the need for a more general probabilistic model. For the sake of clarity, we explain our observations based on a single LJ state-point and then elaborate on the effects of density and temperature variations on the above parameters.

The paper is organized as follows. An outline of the simulation methodology and the Molecular Dynamics model is given in Section 2. In Section 3.1, we use the Navier–Stokes equations to derive an equation for the local density contrast. We show how it is related to the entropy production in the system. In Section 3.2, we explain the fluctuation theorem and the equivalence between the dissipation function and the entropy production. With this information, we show how local density contrast are connected to the shear stress. Owing to the random nature of the shear stress, we derive a general probabilistic description using principles from information theory in Section 3.3. The structural and statistical features of a specific fluid undergoing Couette flow are presented in Section 4. In Section 4.1, we focus on the statistical characteristics of density and shear stress fluctuations. We show how the departure from Gaussian statistics can be used to characterize the linear and nonlinear flow regimes, and identify the critical strain rate at which the fluid starts shear thinning. The effects of variation of fluid density and temperature on the aforementioned characteristics are discussed in Section 4.2. The conclusions and major findings are summarized in Section 5.

2. NEMD simulation

2.1. Method

The problem with simulating homogeneous flows driven by boundaries in real physical systems (e.g., Couette or elongational flows) is that a microscopic simulation explicitly including the walls invariably induces density inhomogeneities