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HYDROMECHANIC THEORY OF ANOMALOUS TRANSPORT: RELAXATION TOWARDS EQUILIBRIUM IN THE ABSENCE OF DISSIPATION

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ABSTRACT

Motivated by the analysis of particle transport in heterogeneous systems, e.g. hydrogels, we consider the statistical and thermodynamic properties of colloidal particles in fluid possessing memory effects in isothermal conditions. The momentum balance equation for a particle of mass m reads

$$m\,\frac{dv(t)}{dt} = -\int_0^t h(t-\tau)\,v(\tau)\,d\tau - \int_0^t k(t-\tau)\,\left(\frac{dv(\tau)}{d\tau} + v(0)\,\delta\tau\right)\,d\tau \tag{1}$$

where $v(t)$ is the particle velocity, $h(t)$, $k(t)$ are respectively the dissipative and fluid inertial kernels, and $R(t)$ is the fluctuating force the statistical properties of which stem from the fluctuation-dissipation relations [1; 2; 3]. The kernel $h(t)$ accounts for the dissipative viscoelastic effects, while $k(t)$ arises from fluid inertial contributions, and corresponds to the generalization of the Newtonian Basset kernel to generic fluids [4].

The fluid-inertial kernel does not contribute to dissipation, that solely depends on $h(t)$ via its integral

$$\eta_\infty = \int_0^\infty h(t)\,dt \tag{2}$$

Two cases occur: 1) if η_∞ is finite, the particle diffusivity can be defined, since the Stokes-Einstein relation for the particle diffusivity D at constant temperature T holds, $D\eta_\infty\, k_B T$, where k_B is the Boltzmann constant; 2) if η_∞ diverges to infinity, particle motion is anomalous and the Generalized Stokes-Einstein relations applies [5].

From the hydromechanic theory of anomalous motion developed recently in [2], there exists also another case that deserves particular attention from the point of view of the thermodynamics of irreversible phenomena.

This is when no dissipation occurs, i.e. $h(t) = 0$, and particle motion is controlled purely by fluid inertial effects. Physically, this could be the case of a superfluid phase at very low temperature. Also in this case, the integrability of the kernel controls the qualitative properties of the dynamics. If $k(t)$ is summable, i.e. if

$$k_\infty = \int_0^\infty k(t)\,dt \tag{3}$$

is finite, no relaxation towards an equilibrium behaviour in the momentum dynamics occurs, and particle motion is ballistic. Conversely if k_∞ is unbounded, in the meaning that $k(0)$ is finite and

$$k(t) \sim t^{-\xi}, \quad \text{for large } t \tag{4}$$

with $\xi < 1$, relaxation towards an equilibrium velocity distribution occurs, and the motion is superdiffusive, i.e.

$$\langle x^2(t)\rangle \sim t^{1+\xi} \tag{5}$$

where $\langle x^2(t)\rangle$ is the particle's mean square displacement. The slowly relaxing tails in $k(t)$ determine the emergence of an apparently dissipative dynamics, and this can be explained by means of the theory developed in [2].

The aim of this presentation is to address the hydromechanic theory of anomalous diffusion, focusing particularly on the case where $\eta_\infty = 0$ and $k_\infty = \infty$, addressing the mathematical physical origin of the occurrence of an equilibrium behaviour and discussing its thermodynamic implications.

KEYWORDS: Brownian hydromechanics, thermalization, anomalous diffusion, dissipation, fluid inertial effects.

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