Chapter 5. Conclusions and recommendations.

A summary of the results contained in this Thesis is given, with an overview of proposals for further research that address some of the open problems in the field.

A number of original results have been presented in this Thesis, in the context of atomic liquids driven by planar elongational and planar shear flows. Firstly, a detailed analysis of chaotic properties for nonequilibrium systems subject to those flows and constrained by a Gaussian thermostat (or ergostat) has been provided. Through a comparison between long time simulations of PSF and PEF samples at the same energy dissipation rate, a proof that the former violates the conjugate pairing rule regardless of system size has been given. Numerical results clearly support the fact that PEF satisfies CPR, as expected from its Hamiltonian nature, with small divergences depending on size and due to fluctuations associated with the Gaussian mechanism. At the density studied, the sum of all positive Lyapunov exponents increases for PEF with the rate of elongation and viceversa for PSF, whereas the dimension of the attractor on to which the phase space collapses is comparable between the two flows, showing dependence on the rate of energy dissipation alone. Secondly, a proof of the independence of molecular dynamics simulations of planar elongation from boundary conditions has been detailed. In the case of large number of atoms, the use of CPR and analytical considerations guided us to infer the invariance of phase space trajectories from initial Kraynik-Reinelt parameters (or equivalent Arnold cat maps). For small systems, the independence of full Lyapunov spectra and a discussion of the exponents related to the conserved quantities in the system completed the demonstration and reinforced the reliability and robustness of the PEF SLLOD algorithm. Furthermore, a procedure for the simulation of this type of flow in a constant pressure and constant temperature system has been devised, and used to compute the nonequilibrium viscosity of an atomic fluid. This ensemble is the one that better captures the setting of most commonly employed experimental techniques on PEF, and our method can be straightforwardly applied to complex molecular liquids for which a host of laboratory measurements exist. Finally, the “new-cell” algorithm has been exploited to compare the Lyapunov spectra of small PEF and PSF atomic systems, providing evidence that the two exponents relative to the degrees of freedom of the Nosé-Hoover barostat pair to zero. This is intuitively expected because the NH equations of motion that constrain the pressure are insensitive to the nonequilibrium contributions present in the underlying atomic dynamics, and because *NpT* and *NVT* phase space trajectories at the "extended" state point (N, p, T, V) are actually identical, giving rise to equal dissipation-related contractions which in turn force the "extra" NH couple of exponents to sum to zero.

As a consequence of the results that we have proposed in this work, many open questions and new directions in the investigation of chaoticity, transport properties and irreversibility for systems driven by PEF arise.

One such topic is the presence, and if so, the characteristics of a "string phase" due to a profile biased thermostat at high rates of elongation, which we repeatedly questioned in the previous Sections. It still remains to be understood what shape these structures might assume and in which direction they might be found, also given that, contrary to PSF, a unique constant plane orthogonal to the direction of the flow for planar elongation does not exist in every point in the space. The fact that the geometry for PEF in the *xy* plane is different from shear might be related to an onset of strings at a higher energy dissipation rate for the former with respect to the latter, and could lead to non trivial stability properties of the artificially ordered lanes. Extracting nonequilibrium viscosity with the adoption of a configurational thermostat allows a comparison with the data obtained with a Gaussian isokinetic method reported in Fig. (2.6) and could give indirect information on the existence of an ordered phase at large $\dot{\varepsilon}$. A computation of the pair correlation function $g(\mathbf{r})$, which measures the average distribution of distances among the atoms in the sample, can help reconstruct the arrangements of particles in the liquid and recognize the emergence of clusters. A direct evaluation of the flow velocity profile according to Eqs. (1.3)-(1.4) should be also required to realize at which rate and how secondary nonlinear contributions start to appear in the flow, causing the assumption that $v_x(\mathbf{r}_i)$, $v_y(\mathbf{r}_i)$ are linear to fail.

Since the models studied in this Thesis are homogeneous, it is interesting to ask how the properties of nonequilibrium systems change when inhomogeneous confinement is considered, in particular regarding the behaviour of oscillations in the thermodynamical observables. As we discussed in Subsection 3.2.2, although fluctuation theorems represent an intensively active field of research, studies on the irreversibility of liquids subject to PEF have not been reported in the literature yet, even though several dissipative phenomena that display similar flow geometry are found in real life. One of these examples of inhomogeneous systems is represented by microporous membranes, which model the essential features of a variety of nanotechnology applications, such as those recently introduced in medicine for immunisation against transplants rejection (Desai *et al.*, 1999a; Desai *et al.*, 1999b). A confined system with porous boundaries, which surround a small number of particles under the action of planar elongation, can be thought of mimicking, for instance, the contraction and dilation experienced by a membrane that is coating a human heart tissue. We believe it is worthwhile to study how the size of the sample, the permeability of the membrane, the spatial inhomogeneities in the phase variables and the elongation field might affect the character of the fluctuations in physical properties such as internal pressure, stress or energy. One of the theoretical questions associated to this approach concerns the universality of recently proposed formulae for fluctuations (see for instance (Bonetto *et al.*, 2006; Baiesi *et al.*, 2007)), whose applicability for every system of interest does not seem to be valid (Harris *et al.*, 2006; Williams *et al.*, 2006). On the practical side, once these fundamental aspects are addressed and the functional dependence of convergence times of nonequilibrium observables is understood for this model, we believe that it will be possible to improve and eventually replace the lengthy and case-dependant calibration process for micromembranes with a more efficient design based on fluctuation theorems, so that these nanodevices will possess the transport properties required by the user.

In our results concerning the phase space contraction presented in Chapter 4, a characterization of the topology of the fractal attractor could not be pursued because of the prohibitively large number of dimensions involved and of the absence of any indication about relevant directions that could be considered as preferential for constructing a Poincaré section. It should also be noted that, at the moment, there are no studies in the literature that involve a very small number of particles under PEF and detail the basic chaotic properties of the system. The fact that PEF, contrary to PSF, displays a

Kolmogorov-Sinai entropy that grows with the applied external rate of perturbation might suggest that there are sensitive differences in those fundamental properties between the flows. Referring to previous investigations by Morriss (Morriss, 1987, 1989) for a two body system under Couette flow, it would be interesting to characterize the coordinate and momentum space distributions for PEF and compare them with their PSF counterparts. We would especially like to see whether for the coordinate distribution of PEF there is a transition similar to the one occurring at $\dot{\gamma} \sim 1.0$ for PSF, which causes a single-peak odd function to become a many-peaks positive function. It would also be worth investigating if the momentum distribution for PEF signals a preferred region for the occurrence of collisions in the coordinate space, as it does for PSF. Analysis of the generalized dimension of the phase space attractor and of the spectrum of singularities as functions of the elongational rate are likely to show discrepancies between the two fields, possibly indicating a different topology for the two attractors that was impossible to grasp in our results for $N = 8$ and $N = 32$ samples.

Among the many other possibilities for further studies, we would like to conclude the Thesis by suggesting two more topics: Lyapunov modes for nonequilibrium systems and the analytical treatment of liquids of hard spheres subject to PEF. In the case of samples at equilibrium, the former have been discussed in Subsection 3.2.2, where we have noticed how these modes convey a profound picture of hydrodynamical features in terms of the chaotic directions actively excited in the system. Hard spheres still constitute a very active field of research, although a host of results have been accumulating in the literature for the past fifty years (Bunimovich *et al.*, 2000), and have recently been the subject of interesting studies for colour conductivity and SLLOD PSF coupled to a Gaussian isokinetic constraint (Petravic and Jepps, 2003; Jepps and Petravic, 2004). We believe that analytical solutions for *N* hard-core bodies under PEF should bring more insight, for instance, into the general stability properties of phase space trajectories, the distribution of collisions and the long time behaviour and size dependence of fluctuations in the system. The analysis of Lyapunov modes for out of equilibrium liquids is still in its early stage of development and, at the best of our knowledge, a contribution regarding hard or soft atomic models under PEF or PSF has not been proposed yet. All these are likely to be promising opportunities for enriching our understanding of nonequilibrium processes and deepening our comprehension of irreversible boundary driven flows.