

Chapter 1

Molecular Simulation of Fluids

This work is the result of research conducted on the molecular simulation of fluids. Traditionally, science, in order to understand the phenomena occurring in nature, used two different approaches: experiment and theory. These two approaches are not necessarily separate. In fact, the ‘art’ of collecting experimental data usually requires profound theoretical knowledge, while on the other hand, models require a necessary minimum amount of experimental data to derive some of their parameters. It is better to view them as complementary approaches that together strengthen the scientific investigation. Molecular simulation, since the advent of the computer, has become an important means of carrying out scientific research.

Despite the commonly used term ‘computer experiments’, molecular simulation belongs to the theoretical approach, unless we intend to investigate a ‘virtual’ reality. We can envisage two main reasons why molecular simulation is associated with the experimental approach. The first reason is a suggestive one and is due to its ability to reproduce the motion of the particles as it occurs in nature. In this regard, even if simulation techniques could reproduce molecular motion in detail, they would be, in any case, a representation of real systems. Moreover techniques that try to simulate closely real systems, show less predictive power than others, which use more artificial implementations. The other reason is more a procedural one. Usually molecular

simulation is used to test the validity of a theory or a theoretical conjecture, or even to discriminate between two theories. While this is indeed true, ultimately it is experiment that will decide the matter.

More interesting, and maybe more speculative, is to consider if molecular simulation is a deductive or an inductive method. The use of semiempirical models, such as for example intermolecular potentials fitted on experimental data, could be indeed indicative of an inductive procedure. However, these models are usually supposed to be applied under a range of conditions wider than those used to derive the models themselves. Furthermore, *ab initio* techniques [Gal93] are meant to predict general behaviour, utilizing very elementary initial assumptions.

The appeal and usefulness of molecular simulation is that it often allows accurate calculation of natural phenomena without the plethora of approximations and assumptions that limit conventional theoretical approaches to prediction and estimation. The key theoretical assumption of molecular simulation is to envisage any physical system as a collection of particles. In general, all the macroscopic properties such as temperature, pressure and density can be related to the motion or the state of these particles. Consequently, knowing the motion or the state of the particles enables one to deduce the macroscopic properties of the system. From a *classical* dynamics viewpoint, to derive the motion of a collection of particles it is required to know the forces acting on them. One may then use Newton's equations of motion to solve for the particle positions and momenta. From a statistical mechanics viewpoint, the knowledge of the state of an ensemble of particles is related to the energy of the particles, which allows the derivations of probabilities relative to that state.

Molecular simulation techniques, therefore, require the adoption of an intermolecular potential to represent the interactions between the particles of any physical system

(solid, liquid or gas). The intermolecular potential and a limited number of approximations, represent the model of a physical system that is used to test against experimental data or preexisting theoretical models. The computer generates either the motion or different states of the particles, and the average values of the physical quantities of interest can be calculated. The two main molecular simulation techniques, *molecular dynamics* (MD) and *Monte Carlo* (MC) techniques [All87, Hey98], implement these ideas. The first follows a dynamical approach, utilizing Newton equations of motion, the second a statistical mechanics approach, using the concept of configuration space. Nowadays these techniques have reached such a level of sophistication that they are able to reproduce experimental results with good accuracy [Ant97, Buk01].

It is commonly assumed that intermolecular interactions are confined to pairs of molecules [Pan87, Pan88, Pla97, Sad96a], and contributions involving three, four or more atoms are ignored. When this assumption is invoked, the molecular properties are assumed to be ‘pair-additive.’ Generally, interactions between pairs of molecules make the overwhelming contribution to the overall intermolecular interaction. However, it is also documented [Elr94] that three-body interactions can make a significant contribution to intermolecular interactions in liquids, (see Chapter 2). Despite this, molecular simulations rarely account rigorously for the effect of three-body interactions [Sad96b, Sad98a, Sad98b, Sad98c, Ant97]. Instead, the typical molecular simulation assumes pair additivity, and uses a simple ‘effective’ intermolecular potential in which many-body effects are said to be included in the values of the intermolecular parameters.

In the following sections we summarize the aims of our work (section 1.1) and give a brief account of the background and progress in molecular simulation regarding the topics we investigated (section 1.2 and 1.3).

1.1 Aims

The aim of this work is to use molecular simulation to investigate the role of three-body interatomic potentials in noble gas systems for two distinct phenomena: phase equilibria and shear flow. In particular we studied the vapour-liquid coexisting phase for pure systems (argon, krypton and xenon) and for an argon-krypton mixture. We also studied the dependence of the shear viscosity, pressure and energy with the strain rate in planar Couette flow. We give here a brief review of the previous work in these fields to better delineate our task. The rest of the thesis is arranged as follows: in Chapter 2 we give details of the interatomic potentials and of the techniques used. In Chapter 3 and Chapter 4 we report the results obtained for phase equilibria and planar Couette flow simulations respectively. Chapter 5 contains our conclusions and recommendations.

1.2 Background

Previous work [Sad96b, Ant97, Sad98a] regarding the role of three-body interactions on the phase behaviour of pure atomic systems has been restricted to the Axilrod-Teller term [Axi43] and the calculations have been confined mainly to argon. In addition, calculations on the influence of three-body interactions on phase behaviour of some theoretical binary mixtures are also available [Sad98b, Sad98c]. Sadus and Prausnitz [Sad96b] reported that the Axilrod-Teller term contributes typically 5% of the overall energy of the liquid phase of argon. Calculations for the vapour-liquid coexistence of argon by Anta et al. [Ant97] and Sadus [Sad98a] using a combination of the Lennard-

Jones and Axilrod-Teller potentials indicate that the inclusion of three-body interactions deteriorates the agreement between theory and experiment for the coexisting liquid phase densities. This failure can be attributed to the effective nature of the Lennard-Jones potential (see Chapter 2). The use of ‘effective’ intermolecular potentials is a source of considerable inaccuracy and uncertainty in molecular simulations. For example, in Chapter 3 we show that three-body interactions contribute significantly to the phase behaviour of fluids, whereas this effect had been hidden previously by the use of effective intermolecular potentials. The agreement between experiment and theory for the phase envelope is improved considerably by explicitly accounting for three-body interactions. However, accounting for three-body interactions requires considerably more computing resources than simple pair interactions. In the worst case, the computing time of a system of N molecules scales in proportion to N^2 for pair interactions, compared with N^3 for three-body interactions. Although computation-time saving algorithms have been developed [Sad99, see also Appendix 2] to avoid the worst case scenario, accounting for three-body interactions typically requires at least one order of magnitude more computing time than simple pair calculations. This means that such calculations are far from routine, even with today’s high performance computers. However, because of the importance of three-body interactions, it is highly desirable to include them in molecular simulations.

Anta et al. [Ant97] reported good results for vapour-liquid coexistence of argon using the Aziz-Slaman [Azi86, Azi93] potential in conjunction with the Axilrod-Teller term. Unlike the Lennard-Jones potential, the Aziz-Slaman potential is a genuine pair potential and it is thought to be the best representation of the two-body interactions for argon. However, its mathematical expression is rather complicated. For argon we used the Barker-Fisher-Watts (BFW) potential [Bar71a], for computational convenience and

because equivalent expressions are available for krypton and xenon. We also show in Chapter 3 that the Aziz-Slaman potential and BFW potential produce similar results for the argon vapour-liquid coexisting curve.

Non-equilibrium molecular dynamics (NEMD) simulations of Couette flow (see Chapter 2) are commonly reported using either the Lennard-Jones or Weeks-Chandler-Anderson (WCA) intermolecular potentials to describe interatomic interactions [Eva90, Sar98]. However, both the Lennard-Jones and WCA potentials are effective multi-body potentials and as such they do not represent two-body interactions accurately [Bar76]. Earlier simulations [Eva80, Eva81] with these potentials appear to confirm the non-analytic dependence of viscosity (η) with shear rate in the limit of low strain rate ($\dot{\gamma}$). However, more recent work questions the $\dot{\gamma}^{1/2}$ dependence of the shear viscosity. For example, Ryckaert et al. [Ryc88] and Ferrario et al. [Fer91a] found a $\dot{\gamma}^2$ dependence of the shear viscosity. The significance of these results is unclear because of the high strain rates and large statistical uncertainties in the data [Tra98]. Furthermore, using profile biased thermostats, namely thermostats that make some assumption about the form of the streaming velocity profile [Eva90], under conditions of large strain rates, can induce unwanted string-phases in the fluid, which consist of highly ordered solid-like configurations [Erp84]. This significantly reduces both the shear viscosity and the hydrostatic pressure from their true values [Eva86, Eva92]. Bhupathiraju et al. [Bhu96] demonstrated that in the limit of zero strain rate the shear viscosity behaves in a Newtonian manner, i.e., the shear viscosity becomes independent of $\dot{\gamma}$. Travis et al. [Tra98] showed that the shear viscosity may be fit by a number of functions that do not have any theoretical basis. They also showed that the viscosity profile may be successfully fit by two separate linear functions of $\dot{\gamma}^{1/2}$ in two different strain rate regimes. Alternatively a Cross equation [Cro65], or the Quentrec local-order theory for

isotropic fluids [Que82, Tro84] were also found to give reasonable agreement with simulation data.

Of particular relevance for our current work is the mode-coupling theory [Kaw73] which predicts that in the limit of zero shear rate the shear viscosity is a non-analytic function of the strain rate, $\eta \approx \dot{\gamma}^{1/2}$. This theory also predicts that the hydrostatic pressure varies as $\dot{\gamma}^{3/2}$. Mode coupling theory does not provide guidance on how small the strain rate must be in order to observe the predicted $\dot{\gamma}^{1/2}$ and $\dot{\gamma}^{3/2}$ dependence for the shear viscosity and hydrostatic pressure, respectively. As NEMD simulations are typically performed at relatively high rates of strain to obtain high signal to noise ratios, such simulations cannot confirm the predictions of mode coupling theory. In the absence of simulation data at field strengths several orders of magnitude smaller than those typically achievable, the question of the validity of mode coupling theory remains open. However, most previous NEMD simulations using effective multi-body intermolecular potentials have shown that the hydrostatic pressure and internal energy *do* behave as predicted by the theory, even at these relatively high strain rates.

We are aware of only one previous NEMD study of simple atomic fluids interacting via accurate two- and three-body intermolecular potentials. Lee and Cummings [Lee94] reported NEMD simulations of planar Couette flow for a system of 108 atoms interacting via a potential composed of the Barker-Fisher-Watts two-body potential [Bar71a] plus the three-body triple-dipole potential of Axilrod and Teller (AT) [Axi43]. The three-body interaction was observed to reduce the value of the shear viscosity by only 3%. In the range of strain rates studied, Lee and Cummings found that the strain rate behaviour of the energy, pressure and shear viscosity all conformed to the predictions of mode coupling theory.

1.3 Progress in molecular simulation

Phase equilibria

It is found by experiment that only a certain number of the physical properties of a substance can have arbitrary values. The remaining properties are determined by the nature of the system. For example, considering a gas at temperature T with a given mass m and held in a container of volume V , the value of its pressure P can be obtained via an equation in m , V and T ;

$$f(P, m, V, T) = 0 \quad (1.1)$$

such an expression is known in general as the equation of state [Sea75]. In this work we are interested in thermodynamic systems, the state of which can be determined by properties like density, temperature, pressure, chemical potential, etc. The phase of the system, namely gas, liquid or solid, is an important characteristic and in particular phase transitions represent an important field of study. Both technological and scientific applications require a detailed knowledge of phase behaviour of fluids and their mixtures. For example, chemical industries need to know transition phenomena and the relative parameters (critical temperatures, pressures, etc.) to separate particular substances from their original mixtures. This wide interest is demonstrated by the large amount of experimental data [Wic73] collected and the number of semiempirical and theoretical models proposed regarding phase equilibria. Despite the substantial knowledge so far gained much more remains to be learned. For example, multicomponent mixture experiments are very rare and performed in limited temperature and pressure ranges because of their high realization costs [Gub89]. Significant information comes from equation-of-state models [San94], but they can not

be used to accurately predict properties outside the range of experiments adopted to obtain the parameters of the models.

In this regard, molecular simulation represents a complementary method [Gub96, Qui01]. Utilizing intermolecular potentials obtained from either quantum mechanics or semi-empirical calculations, and adopting fewer approximations, molecular simulation can be applied over a wider range of conditions. In fact, even if their parameters are determined from particular experimental data, they can be used under more general conditions [Bar76]. Here we give a brief description of some of the molecular simulation techniques dedicated to phase equilibria. For further details we refer to the following reviews in the literature [Gub89, All93, Pan94a, Pan95, Fre96, Pan00].

The most direct procedure to simulate phase equilibria may simply consist of adequately changing the temperature or the pressure of the system and observing the occurrence of a phase transformation. This is possible via either Monte Carlo or molecular dynamics methods. Reviews of these techniques were given by Rowlinson and Widom [Row82] and by Gubbins [Gub89]. Unfortunately, important difficulties characterize these direct methods. First-order transitions [Hua63] may show hysteresis due to a large free energy barrier separating the two phases at or near to the coexistence [Fre96]. This free energy barrier consists of the free energy of the interface. The larger the area of the interface, the higher the barrier. In a normal simulation, even with large size systems, a significant number of particles are in the proximity of the interface, which can alter the outcomes of the simulation. Long equilibration times are required and it is very difficult to maintain the coexisting phases when the two values of the densities are similar. On the other hand, the direct methods do not require random particle exchanges as other techniques do [Pan00], in order to achieve the equality of the chemical potentials (material equilibrium) in the coexisting phases. For systems with

high densities the direct method would be preferable, since particle insertions are characterized by low probabilities. However, the material equilibrium by diffusion through the interface requires long simulation times under high density conditions [Yan96]. Despite these deficiencies, the direct methods provide useful information regarding the interface properties and surface tension.

Simulating the phase coexistence without interfaces is the basic and innovative idea of the Monte Carlo (MC) Gibbs ensemble method introduced by Panagiotopoulos [Pan87, Pan88]. As discussed in more detail in Chapter 2, the coexisting phases take place in separate simulation boxes. Importantly, material equilibrium between the different phases is achieved by exchanging particles between the boxes. This also represents the weakness of the method. The higher the density of at least one phase, the lower is the probability to successfully exchange the particles. Molecular dynamics (MD) implementation of the Gibbs ensemble method was proposed by Palmer and Lo using an extended system Hamiltonian [Pal94]. Baranyai and Cummings [Bar95] reported a simpler version of the MD Gibbs ensemble, using Hoover-type equations of motion [Mel93, Mel94] and particle exchanges like in the traditional MC version [Pan88]. The MD versions are able to well reproduce the results from MC Gibbs ensemble simulations. Other versions of the technique are reviewed in the literature [Pan95, Fre96, Pan00]. In particular, for multisegment or polymeric systems, versions of the Gibbs ensemble, using biased sampling methods for particle insertion, have been proposed [Sie93, Smi95, Fre96]. Also parallel versions were presented [Loy95, Ess95, Str00]. In general, the Gibbs ensemble technique is easy to implement and can be used to get information on the properties of coexisting phases from a single simulation.

Material equilibrium is achieved when the chemical potentials of all the coexisting phases are equal. Methods for calculating the (excess) chemical potential via molecular

simulation are available [Wid63, Kof97, see also Chapter 2]. The chemical potential can be calculated also from grand canonical Monte Carlo simulations [Fre96]. Performing several canonical simulations with, for example, Widom test particle insertions [Wid63] or grand canonical Monte Carlo simulations, it is possible to determine curves of the chemical potential as a function of the pressure for the different phases of interest. The coexisting condition is found at the point of intersection of the curves [Pan94a]. Möller and Fischer [Möl90] and Lotfi et al. [Lot92] used this scheme and calculated with high accuracy the coexistence properties of pure Lennard-Jones fluids. For multicomponent systems and for pure systems near the critical point this scheme requires a significant number of simulations [Pan94a], hence other techniques are preferable.

A method that does not require the equilibration or the calculation of the chemical potential of the coexisting phases, is the Gibbs-Duhem integration introduced by Kofke [Kof93a, Kof93b]. This method for pure systems consists of the numerical integration of the (first-order nonlinear) Clausius-Clapeyron differential equation [Fre96]:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (1.2)$$

where ΔH and ΔV are the differences of the enthalpy and volume in the two phases respectively. The method requires the knowledge of a coexisting point at a given temperature and pressure, which can be obtained using other techniques. A complete phase diagram is then determined by integrating Eq. (1.2), usually by a predictor-corrector method [Gea71]. Standard molecular simulations are used to calculate the right-hand side of Eq. (1.2) relative to infinitesimal and consecutive changes in the temperature. This method was applied for vapour-liquid [Kof93a, Kof93b] and solid-liquid coexistence [Agr95] of the Lennard-Jones fluid and for vapour-liquid coexistence of the two-centre Lennard-Jones fluid [Lis96a]. For multicomponent fluids, Gibbs-Duhem integration has to use particle exchanges, but exchanges can be avoided for one

component, usually the one most difficult to be exchanged. Lisal and Vacek used Gibbs-Duhem integration for mixtures of two-centre Lennard-Jones fluids [Lis96b]. Even though numerical errors in the integration and inaccuracy of the initial coexisting point may lead to deviations from the actual phase diagram, the method is very reliable, and for the solid and highly structured phases is the most efficient among the other techniques.

In a standard Monte Carlo technique, averages of the thermodynamics quantities are calculated for the parameters chosen in the simulation. For example, to obtain values of thermodynamic quantities relative to a number of different temperatures, an equivalent number of simulations have to be performed. Ferrenberg and Swendsen envisaged a method [Fer88] that, considering only a single simulation at given values of some parameters, allows calculating the thermodynamic quantities for different values of those parameters. This concept was first applied with the Ising model [Fer88, Fer89, Dru96], using multipole histogram techniques to collect data at different points of the parameter space in order to calculate a distribution for the density of the states. The same scheme, known as histogram reweighting methods, can be used for continuous-space fluids. Details of how this procedure can be applied for phase equilibria of pure and multicomponent systems are given in the references [Wil95, Pot98, Pot99, Pan98, Pan00]. The histogram reweighting methods show better accuracy in comparison with the Gibbs ensemble [Pot98] for a given amount of computer time, and they are more reliable in deriving critical points in conjunction with finite-size formalism [Pot98]. The disadvantages of these methods are that their implementation requires more effort and their efficiency decreases rapidly with increasing system size.

Considering that we wanted to study the vapour-liquid equilibria of fluids with relatively complex intermolecular potentials requiring a reasonable accuracy, the choice of the Gibbs ensemble method suited our needs best.

Transport phenomena

Statistical mechanics devoted to equilibrium systems provides, using a molecular description, phase averages of macroscopic quantities such as for example pressure and specific heat. These phase averages are obtained through probabilistic assumptions, associating a probability to each state of the system and using analytic tools for the construction of asymptotic formulae [Khi49].

Viscous flow and thermal conduction phenomena are examples of non-equilibrium systems. They are usually called transport processes. The transport properties of atomic or molecular fluids under shear are of significant scientific and technological interest. The dependence of the shear viscosity (see Chapter 2) as a function of applied strain rate is of major importance in the design of suitable lubricants, and the viscoelastic properties of polymer melts under extensional and shear flows is important to the industrial processing of plastics. The structural design of molecules under appropriate flow fields can be aided by application of simulation methods such as non-equilibrium molecular dynamics [Eva90, Dai92]. In addition, NEMD can also be used to assess rheological models such as the Rouse or Doi-Edwards models of viscoelasticity for polymer solutions and melts [Doi86], or the mode-coupling theory of Kawasaki and Gunton [Kaw73].

Shear viscosity is one of the Navier-Stokes transport coefficients [Eva90], which relate thermodynamic fluxes to their conjugate thermodynamic forces. Fluid mechanics is able to determine the macroscopic behaviour of non-equilibrium systems, but its laws

need to be supplemented with the specification of adequate boundary conditions and with thermophysical constants like the above mentioned transport coefficients. These quantities are usually obtained through experiments. One of the aims of statistical mechanics, devoted to non-equilibrium systems, is to derive these quantities from a microscopic description of the system. For dilute gases, kinetic theory [Hey98] is able to provide values of the transport coefficients in excellent agreement with the experimental data [Bar71b]. Unfortunately, this theory can not take account of higher density fluids. It has been proved that Navier-Stokes transport coefficients are non-analytic functions of the density [Dor70, Dor72], which means that a power-series expansion is not possible.

Kubo [Kub57] demonstrated that a *linear* transport coefficient can be determined through the equilibrium fluctuations of the relative flux. For example, the (Green-Kubo) relation for shear viscosity, \mathbf{h} , in the limit of zero shear rate is:

$$\mathbf{h} = \frac{V}{k_B T} \int_0^{\infty} \langle P_{xy}(0) P_{xy}(t) \rangle dt \quad (1.3)$$

where $-P_{xy}$ is the shear stress, k_B is the Boltzmann constant and $\langle \rangle$ represents an equilibrium ensemble average. Eq. (1.3) and the equivalent Green-Kubo relations [Eva90] for the remaining transport coefficients can be calculated via equilibrium molecular dynamics simulations. Time correlation functions, like Eq. (1.3), are the average response of system properties to spontaneous fluctuations, which are consequently very small. The signal-to-noise ratio is poor at long times, which may give an important contribution to the integral in Eq. (1.5) or in the Green-Kubo relations for other transport coefficients. Furthermore, the finite size of the system limits the time the correlation functions can be calculated for [All87, Hey98]. To counter these limitations NEMD techniques were invented, in which the response of the system to an *induced*

perturbation is calculated. The perturbation the system experiences is larger and consequently the signal-to-noise ratio is improved. Furthermore, these techniques can consider the steady state response to the perturbation, thus the long-time behaviour of correlation functions is avoided.

A common practice to generate a non-equilibrium state in a molecular simulation, for example to induce a momentum or energy flow, is to introduce in the simulation cell boundary regions which act on the particles as momentum or energy reservoirs. The idea behind these techniques is to simulate closely what occurs in real systems. For this reason they are called ‘realistic’ techniques. For example Ashurst and Hoover [Ash73, Ash75] simulated planar Couette flow using fluid-like sliding walls [Lie92] and calculated the Lennard-Jones fluid shear viscosity. Tenenbaum et al. [Ten82] used stochastic boundary conditions to simulate the contact with thermal walls. These methods can not use full periodic boundary conditions, therefore they are characterized by surface effects and inhomogeneities in the thermodynamic properties of the fluid. Lees and Edwards developed periodic boundary conditions [Lee72], which enable one to simulate homogeneous planar Couette flow in which the low-Reynolds-number velocity profile is linear [Eva90].

A different approach to simulate a non-equilibrium system consists in altering the standard equations of motion, introducing ‘artificial’ mechanical fields, which exert the perturbation on the systems [Hoo80, Eva84c, Eva90]. Techniques adopting this concept are called ‘synthetic’. Importantly, they do not suffer from surface effects and spatial inhomogeneities. Since the mechanical fields exert work on the systems, which is converted into heat, adequate thermostats have to be used [Hoo85, Eva90] to avoid heating up the system. Gosling et al. [Gos73] used a spatially periodic field to simulate a system under a sinusoidal transverse force and calculated the viscosity utilizing an

extrapolation to infinite wavelengths of the induced velocity profile. They did not use a thermostat, but they adopted an adequately small amplitude of the force, which avoided the temperature rising too rapidly. A further step in this direction is represented by the techniques adopting non Hamiltonian dynamics [Eva90]. For example, for a Nosé-Hoover [Hoo85] thermostat, the particles of the system are weakly coupled to a thermal reservoir, which can add or remove kinetic energy. This is achieved introducing an extra term in the acceleration equations. The resulting equations of motion can not be derived from a Hamiltonian. The Evans-Gillan equations of motion for heat flow [Eva90] are a modification of the standard equations of motion obtained with the introduction of a synthetic field acting on each particle. This synthetic field reproduces the effect on the system of a real temperature gradient. No Hamiltonian is known which is able to generate the Evans-Gillan equations of motion. Both Gaussian [Eva90] and SLLOD [Eva90] equations of motion, which are described in detail in Chapter 2, can not be derived from any Hamiltonian.

Green-Kubo relations can be applied not only at equilibrium, but also to adiabatic linear (weak fields) response theory [Eva90]. When thermostats are used, to keep for example the kinetic energy constant, equivalent relations can be obtained to calculate the transport coefficients [Eva90]. Evans and Morris [Eva84a] showed that time correlation functions using either Newtonian or Gaussian isothermal equations of motion for Navier-Stokes transport coefficients like shear viscosity, self diffusion coefficient and thermal conductivity, are equivalent in the large-system limit.

A further advantage of NEMD techniques is that they can be used to study the non-linear response of systems, where the Green-Kubo relations can not be used. For strong fields, the transport coefficients can be obtained directly by relating the thermodynamic fluxes to the relevant thermodynamic forces. In the NEMD SLLOD technique for planar

Couette flow, the viscosity is derived via the ratio of the shear stress to the strain rate (see Chapter 2). It is noteworthy to point out that this direct method can not be applied efficiently for weak fields because of the deterioration in the signal to noise ratio.

The most efficient way to calculate the transport coefficients in the small field regime is to use ‘synthetic’ NEMD techniques in conjunction with the transient-time correlation function (TTCF) relations [Eva90]. As Green-Kubo relations extract transport coefficients from fluctuations of microscopic fluxes at equilibrium, similarly, TTCF relations extract them from fluctuations of microscopic fluxes arbitrarily far from equilibrium. TTCF can be applied to genuinely non-linear transport processes. Moreover, TTCF relations in the linear response regime reduce to the Green-Kubo relations [Eva90]. It has been shown also that the TTCF and NEMD direct method lead to the same results for strong fields. The subtraction response method [Cic75, Cic76, Cic79] can also be applied in the small field regime, but it has been demonstrated that TTCF is in general preferable in the long time limit [Eva90].