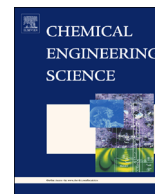




ELSEVIER

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

System size effects on calculation of the viscosity of extended molecules

Stefano Bernardi^a, Sarah J. Brookes^{b,c}, Debra J. Searles^{a,d,*}^a Centre for Theoretical and Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Qld. 4072, Australia^b Queensland Micro- and Nanotechnology Centre, Griffith University, Brisbane, Qld. 4111, Australia^c School of Biomolecular and Physical Sciences, Griffith University, Brisbane, Qld. 4111, Australia^d School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Qld. 4072, Australia

HIGHLIGHTS

- We demonstrate the effect of simulation size on calculation of the viscosity of extended molecules.
- We discuss different approaches to calculation of the shear viscosity of bulk fluids.
- Results of nonequilibrium molecular dynamics simulation of the response of the shear stress to applied strain are presented.
- We identify how to improve the results of simulation of the viscosity in small systems.

ARTICLE INFO

Article history:

Received 6 May 2014

Received in revised form

7 August 2014

Accepted 13 August 2014

Available online 27 August 2014

Keywords:

Molecular dynamics simulation

Viscosity

Nonequilibrium systems

ABSTRACT

We consider finite size effects on calculation of the viscosity of bulk molecular fluids using molecular dynamics simulations. The results are obtained using equilibrium simulations, direct calculations from nonequilibrium molecular dynamics simulations and calculations of the transient time correlation function expression, based on the dissipation theorem for nonlinear response. As with atomic fluids, strain induced by the periodic boundary conditions on the molecular systems can become significant for small systems at high densities and low temperatures. In addition to this effect, the dissipation function has a finite size contribution below a critical size, and this becomes more important as the system size is reduced and the length of the molecule increases. In this paper we show how calculations can be carried out to obtain convergence to bulk values with limited system size simulations.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

In order to make molecular dynamics simulations of bulk systems feasible or efficient, it is necessary to use periodic boundary conditions (PBCs) where a finite number of particles in a unit cell are replicated. The periodicity of these systems still results in finite size effects, however they are reduced compared to those that would be caused by the presence of walls. There is extensive literature on finite size effects on simulation results (see, for example, Denton and Egelstaff, 1997 and Roman et al., 2008, and references therein). With an increase in computational power, the size and complexity of the molecules that can be studied is

* Corresponding author at: Centre for Theoretical and Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Qld. 4072, Australia.

E-mail address: d.bernhardt@uq.edu.au (D.J. Searles).

increasing. However, although some of the finite size effects are sensitive to the number of atoms, others will be sensitive to the number or length of the molecules. In those cases, although the system might be relatively large in size with a large number of atoms, finite size effects might still be apparent.

Some system size effects are simply a result of the inability of the system to explore the full phase space of the bulk fluid, and in many cases the only way to overcome this is to increase the size of the system. Other effects occur due to the fact that the exact expression for the property of interest in a small system differs to that in the bulk system due to the inclusion of finite size terms. In some cases if the expressions are corrected to include these terms, better agreement with the bulk system results will be obtained. This might circumvent the need to increase the system size, and lead to better results without adding significant computational cost and therefore improve the efficiency of the simulation. It is these cases that we are most interested in here.

One important property that can be obtained from molecular simulations is the viscosity of a molecular fluid. Determination of viscosities is of interest in fluidics, rheology and tribology, where long extended molecules may exist at high densities. Under shear, the viscosity of the fluid can increase or decrease and the structure of the fluids can change substantially. As the complexity of the molecule increases, nonlinear response to an applied field occurs at lower strain rates. This is an important issue in NEMD simulations as the strain rates required to get satisfactory signal to noise ratios in the stress are large compared to standard experimental conditions. To overcome this problem, expressions such as the transient time correlation function (TTCF) expression (Evans and Morriss, 1988, 1990) have been developed, and this will be discussed below. In the current manuscript we will focus on calculations of the viscosity of dense fluids.

Finite-sized effects will be considered in three approaches to calculation of the viscosity: equilibrium calculations using the Green–Kubo (GK) expression; nonequilibrium calculations where the strain dependent viscosity can be determined directly from the ratio of the stress to the strain rate (Direct) and nonequilibrium calculations where the strain dependent viscosity is determined from the integral of a TTCF (Evans and Morriss, 1990). Most work on finite size effects on viscosities has considered small molecules at system sizes where the effects are minimal (Yeh and Hummer, 2004). However, Petravac and Evans (1998a, 1998b) and Petravac (2004a, 2004b, 2004c, 2005) have extensively studied these issues for fluids comprised of monatomic Lennard–Jones or Weeks–Chandler–Andersen (Weeks et al., 1971) particles, and have shown how in sufficiently small systems finite size effects are significant. In this paper we extend that work to consider molecular fluids.

2. Calculation of viscosity

2.1. Viscosity from equilibrium simulations

Green–Kubo relations using equilibrium molecular dynamics simulations provide the most common approach for calculation of viscosity. Normally the equilibrium periodic system will comprise of square (2D) or cubic (3D) periodic cells, although when large molecules are considered other shapes might be preferable (see, for example, Wassenaar and Mark, 2004). In addition, the cells are normally aligned as shown on the left of Fig. 1. However, if the periodic cells are shifted in one direction, as on the right of Fig. 1, the strain caused by the boundary conditions produces a non-zero stress. This was demonstrated by Petravac (2004a) for a Lennard–Jones

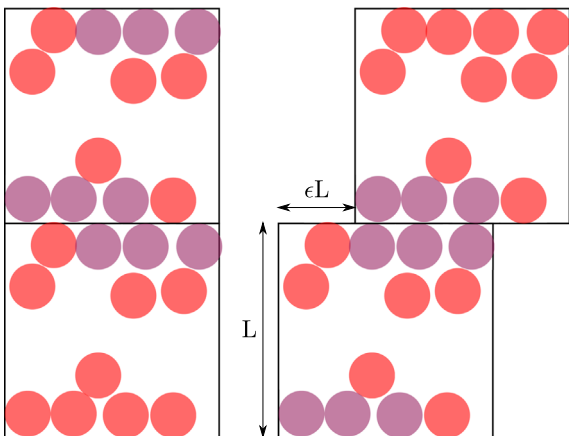


Fig. 1. Schematic diagrams illustrating the strain introduced by shifting the lattice. The simulation cells are aligned in the figure on the left, and are shifted by ϵL in the figure on the right.

atomic fluid. This effect is system size, temperature and density dependent becoming more pronounced as the system approaches the solid-state transition (Petravac, 2004b, 2005). The usual Green–Kubo expression for the viscosity, η , is

$$\eta = \beta V \int_0^{\infty} \langle P_{xy}(0)P_{xy}(t) \rangle_{\epsilon_0} dt, \quad (1)$$

where $\beta = 1/(k_B T)$, V is the volume of the periodic cell, and $-P_{xy}$ is the shear stress. $\langle \dots \rangle_{\epsilon_0}$ refers to an equilibrium ensemble average for a system of periodic cells of length L that are shifted by an amount, Δ along the x -direction to give a dimensionless strain of $\epsilon_0 = \Delta/L$ (Petravac, 2004b). Petravac (2004b) showed that unless ϵ_0 takes on particular values (e.g. $\epsilon_0 = 0$), this expression will diverge, and needs to be modified (Petravac, 2004c) to give a strain dependent form:

$$\eta(\epsilon_0) = \beta V \int_0^{\infty} \langle (P_{xy}(0) - \langle P_{xy} \rangle_{\epsilon_0}) P_{xy}(t) \rangle_{\epsilon_0} dt. \quad (2)$$

2.2. Viscosity from non-equilibrium simulations using direct calculations

In NEMD simulations, the effect of the application of shear to a system is modelled directly, and the ratio of the stress developed in the system to the strain rate applied will give the shear viscosity. The use of NEMD approaches for calculation of transport properties is becoming more widely used, especially with the incorporation of these techniques into readily available software such as LAMMPS (Plimpton, 1995) and RUMD (2014). The utility of these computational techniques includes the determination of the linear transport coefficients for slowly relaxing systems where convergence of Green–Kubo integrals is slow, and for determination of the nonlinear transport coefficients.

The most rigorous approach to model homogeneous planar shear flow is to use the SLLOD equations of motion in conjunction with compatible boundary conditions such as the Lees–Edwards PBCs or the equivalent Lagrangian rhomboid PBCs (Evans and Morriss, 1990). The equations of motion for a system subject to a strain rate, $\dot{\gamma}$, are as follows:

$$\begin{aligned} \dot{\mathbf{q}}_{i\alpha} &= \mathbf{p}_{i\alpha}/m_{i\alpha} + \dot{\gamma} q_{y_i} \\ \dot{\mathbf{p}}_{i\alpha} &= \mathbf{F}_{i\alpha} - \dot{\gamma} \frac{m_{i\alpha}}{M_i} p_{y_i} - \xi \frac{m_{i\alpha}}{M_i} \mathbf{p}_i, \end{aligned} \quad (3)$$

where $\mathbf{q}_{i\alpha}$ is the position of atom α in molecule i , $\mathbf{p}_{i\alpha}$ is its peculiar momentum (the total momentum less the streaming momentum), $m_{i\alpha}$ its mass and $\mathbf{F}_{i\alpha}$ is the total force on the atom due to all inter- and intramolecular interactions. The centre of mass and peculiar momentum of the i th molecule is denoted by \mathbf{q}_i and \mathbf{p}_i , respectively, so q_{y_i} is the y -coordinate of the centre of mass of the i th molecule and p_{y_i} is its centre of mass peculiar momentum in the y -direction, and M_i is the mass of molecule i . The last term in the equation of motion for the momentum is the thermostating term that is applied to prevent the system from heating up, and to allow it to come to a steady state. In this work, a Gaussian thermostat is applied (Evans and Morriss, 1990) to keep the molecular kinetic energy constant, $\frac{1}{2} \sum_i \mathbf{p}_i \cdot \mathbf{p}_i / M_i = \text{const}$,

$$\xi = \frac{\sum_i (\mathbf{F}_i - \dot{\gamma} p_{y_i}) \mathbf{p}_i / M_i}{\sum_i \mathbf{p}_i \cdot \mathbf{p}_i / M_i}. \quad (4)$$

There is some choice in the equations used – e.g. molecular SLLOD where the same streaming velocity is assumed for all the atoms of a molecule, and atomic SLLOD where each atom's streaming velocity is based on its position in the y -direction. In addition, the molecular or atomic peculiar kinetic energy can be thermostatted. These issues have been discussed in detail (see for example, Allen,

Download English Version:

<https://daneshyari.com/en/article/6590893>

Download Persian Version:

<https://daneshyari.com/article/6590893>

[Daneshyari.com](https://daneshyari.com)