

Oscillatory Molecular Dynamics Simulation to extract Dilatational Rheological properties of a Lennard-Jones Fluid

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Abstract: A Molecular Dynamics simulation is developed to measure the dilatational (compression) rheological properties of a fluid and is demonstrated with the Lennard-Jones 12-6 atomic fluid. Small amplitude, oscillatory volume changes imposed on the fluid result in an oscillatory pressure response, from which the complex dilatational modulus is computed. A frequency sweep at low strain amplitude shows that the LJ fluid is elastic dominant with an elastic compression modulus that compares well to the values obtained from equilibrium pressure-density isotherms, computed here and in literature.

I. INTRODUCTION

The bulk compressional or dilatational modulus of a material is a measure of a materials resistance to a compression or a dilatational strain. Formally, it is defined as:

$$E = \frac{dp}{d \ln \rho} = - \frac{dp}{d \ln V}$$

where p is the pressure, ρ is the density and V is the volume and E is an isothermal quantity.

For a bulk fluid, this property would typically be determined from the equilibrium equation of state, that is, the p - ρ isotherm. However, here it is proposed to extract these properties via imposed dilatational strains on the system, where the volume/density of the simulation varies sinusoidally and the corresponding pressure response is monitored. A Lennard-Jones fluid is chosen to demonstrate this idea. The volume available to the LJ atoms is determined by the distance separating two solid surfaces in the walls. An oscillatory, uniaxial volume change(strain) is imposed on the fluid by moving the position of the walls relative to each other and measuring the pressure in the fluid via calculation of the forces on the walls.

II. METHODS

II.A Simulation Parameters

The simulation is periodic in the y and z dimensions, with a size of $L^* = 5$. The x -dimension is finite, as the fluid atoms are bound by the two implicit walls. The initial distance between the walls is taken to be $8L^*$, in order to reduce any effect the walls have on the fluid. Therefore, the left and right walls are positioned at $x_{w,0}^{*L} = -4 \cdot L^*$ and $x_{w,0}^{*R} = 4 \cdot L^*$. The number of atoms in the simulation is determined based upon the volume of the simulation box and the desired density: $N = \rho^* V^* = \rho^* \cdot 8L^{*3} = 1000\rho^*$.

II.B Potential Energy and Forces

In this study, there are two types of interactions: atom-atom interactions and atom-wall interactions. Interatomic interactions are described using the Lennard-Jones 12-6 potential.

$$U_{ij}^* = 4 \cdot (r_{ij}^{*-12} - r_{ij}^{*-6})$$

The potential is cut and shift such that $U_{ij}^* \left(r_{ij}^* = r_c^* = \frac{L^*}{2} = 2.5 \right) = 0$.

As the dimension normal to the walls is finite and non-periodic, the atom-wall interaction is needed to ensure a no flux boundary condition. Here, the Lennard Jones 9-3 virtual wall potential is used. This potential describes the interaction of a single atom with a semi-infinite wall:

$$U_{9/3,i}^* = \frac{4\pi\rho_s\sigma^3}{3} \cdot \left(\frac{1}{15}(x_i^* - x_{wall}^*)^{-9} - \frac{1}{2}(x_i^* - x_{wall}^*)^{-3} \right)$$

For simplicity, the surface atoms have the same size as the fluid atoms, and with the same interaction energy. It is assumed the surface atoms have a close-packed surface density of $\rho_s\sigma^3 = 0.74$.

The total potential energy is then

$$U = \sum_{i=1}^N \sum_{j=i+1}^N U_{ij}^* + \sum_{i=1}^N (U_{9/3,i}^{*,L} - U_{9/3,i}^{*,R})$$

To determine the pressure in the system, the forces on each wall are first calculated assuming the force the wall exerts on each atom is equal and opposite to the force the atom has on the wall. Explicitly, this is written as $F_{wall}^{*L(R)} = -\sum_{i=1}^N F_{9/3,i}^{*L(R)}$.

The pressure is then determined with the following equation: $p^* = \frac{F_{wall}^{*R} - F_{wall}^{*L}}{2L^{*2}}$.

Finally, during oscillation runs, a Berendsen thermostat is employed at each timestep in order to ensure the total kinetic energy of the system doesn't change drastically upon motion of the walls. The scaling factor for the velocities is given as

$\lambda^2 = 1 + \tau^{-1} \left(\frac{T^*}{T_{inst}^*} - 1 \right)$ with a coupling parameter of $\tau = 100$. In addition, the velocity scaling factor is applied only to the atomic velocities in the periodic dimensions y and z.

II.C Simulation Algorithm

II.C.1 Equilibration and Production Run

The first step of the simulation is to first place atoms on a cubic lattice. The system then undergoes a potential energy minimization via a conjugate gradient algorithm.

Upon giving the atoms random initial velocities and accelerations, the Velocity Verlet Algorithm is used to integrate the equations of motion for the Molecular Dynamics simulation, using a timestep of $dt^* = 0.001$. In the initial run, a velocity rescale algorithm is used to equilibrate the system to the desired temperature for 100,000 timesteps, and rescale frequency of 1000 timesteps. Next, velocity rescaling is turned off to begin the production run used to collect data (potential energy, kinetic energy, and pressure) for 1e5-3e5 timesteps both with and without the thermostat.

II.C.2 Oscillation Run

In the next step of the simulation, we impose a sinusoidal change in the distance between the walls at a chosen reduced frequency f^* on the fluid by updating the positions of the walls at every timestep according to:

$$x_w^{*L}(t) = 4L^* \cdot [-1 + \gamma_0 \cdot \sin(2\pi f^* t^*)], \quad x_w^{*R}(t) = 4L^* \cdot [1 - \gamma_0 \cdot \sin(2\pi f^* t^*)]$$

resulting in a volume/density change in the fluid. For small changes, γ_0 , can be thought of as a dilatational strain.

$$\frac{V^*(t)}{V_0^*} = \frac{\rho_0^*}{\rho^*(t^*)} = 1 - \gamma_0 \cdot \sin(2\pi f^* t^*).$$

The oscillatory dilatation of the fluid induces a pressure change from its equilibrium value,

$$p^*(t^*) = p_{eq}^* + \Delta p^*(\gamma_0, f^*) \cdot \sin(2\pi f^* t^* + \delta)$$

which in general gives a pressure response that may be out of phase with the imposed strain by a phase lag δ .

The complex dilatational modulus, the quantity of interest, consists of an in-phase, elastic component E^{**} and an out-of-phase, or viscous, component E^{*n} ; The modulus is then given by

$$E^{**}(\gamma_0, f^*) = E^{**} + E^{*n} = \frac{dp^*}{d \ln \rho^*} = \frac{d dp^* / dt^*}{d d \ln \rho^* / dt^*} \approx \frac{\Delta p^*(\gamma_0, f^*)}{\gamma_0} \cdot e^{i\delta}$$

The oscillation step is run for 1 or more periods, or $N_{periods} (f^* dt^*)^{-1}$ timesteps. Data is averaged-over and collected every 1000 timesteps, which gives at least 100 data points per period. The pressure response is fit with Matlab to an equation of the form

$$p^*(t^*) - p_{eq}^* = C_0 \cos[2\pi f^* t^*] + C_1 \sin[2\pi f^* t^*]$$

where the constants C_0 and C_1 give Δp^* and δ .

III. RESULTS

III.A Equilibrium equation of state

The base state of the Lennard-Jones fluid for the oscillatory MD simulations was chosen to be $\rho_0^* = 0.7$ and $T^* = 2.0$. To compare the oscillatory results with the equilibrium data, several simulations were performed at different densities in order to construct the $p^* - \rho^*$ isotherm. The measured isotherm compares fairly well to the isotherm reported by Johnson et al (1993), who used 864 atoms and a cutoff of $r_c^* = 4$.

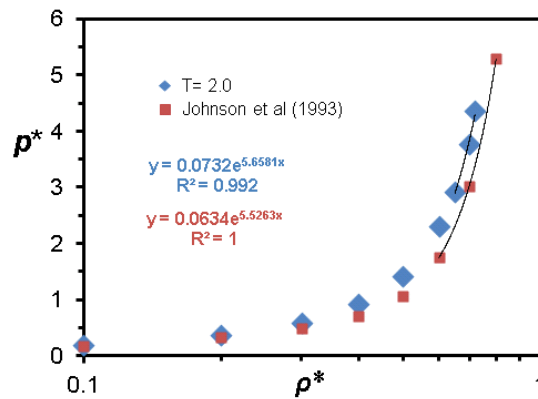


Figure 1: Equilibrium $p^* - \rho^*$ ($T^* = 2.0$) Isotherm

At the target density of 0.7, the measured equilibrium compression modulus is found to be 15.2, which agrees reasonably well to the value of Johnson et al, 11.7 (both obtained here by finding the slope of the $p^* - \rho^*$ data at $\rho^* = 0.7$).

III.B Strain amplitude and Frequency sweep

The first plot shows the normalized, average density and the pressure upon imposing a nominal strain of $\gamma_0 = 0.08$ at a frequency of 0.01. Qualitatively, it can be seen that the initial density increase results in an increase in the pressure. Moreover, the pressure response looks in-phase with the density change, indicating the LJ fluid responds elastically to the dilatational strain. By fitting the response data, the elastic and viscous components of the compression modulus can be calculated. The second graph shows the calculated modulus as a function of strain amplitude. At low strain amplitudes (< 0.1), the modulus is independent of the strain amplitude, indicating the response is linear. Interestingly, the elastic modulus compares quite well to the equilibrium modulus determined from the isotherms. At higher nominal strain amplitudes, the density changes become asymmetric resulting in an asymmetric pressure response that causes the best fit modulus to increase.

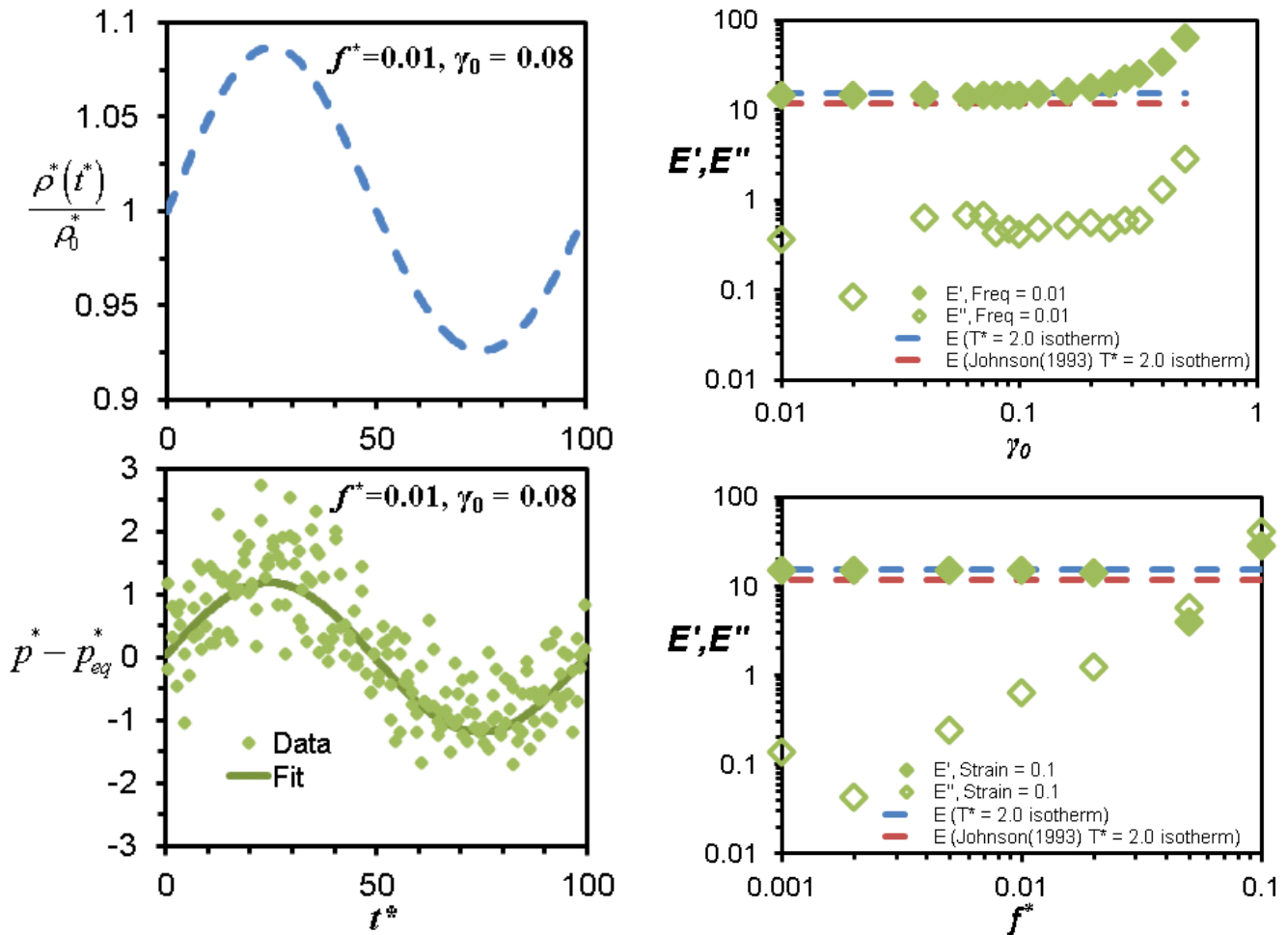


Figure 2: a,b)Density and pressure response upon oscillatory strain; c,d) Complex modulus against c)nominal strain amplitude at fixed frequency $f=0.01$ and against d) reduced frequency at fixed strain amplitude

At a fixed nominal strain amplitude of 0.1, the modulus is measured as a function of the frequency. At low frequencies, the fluid is elastic dominant and agrees with the $f \rightarrow 0$ result from the equilibrium isotherm. Only at relatively higher frequencies is a viscoelastic behavior observed. The cross-over between the elastic and viscous components might indicate a characteristic relaxation time of the fluid.

In summary, the above simulation experiments using Lennard-Jones atoms show that it is possible to extract bulk dilatational mechanical properties of a fluid by moving two bounding walls to create oscillatory volume/density changes and monitor pressure changes. While the Lennard-Jones system may not be the most intriguing system to study, as it is one of the most well understood models, it allows for comparison. Some potential deficiencies in this method could be the difficulty in choosing the right type of atom (molecule)-wall interaction for an arbitrary fluid of interest. In addition, the short timescales of MD simulations would limit the possible frequency range one could explore. Lastly, as bulk fluids typically have high compression elasticity, shear deformations rather than dilatational strains govern most everyday fluid flows.

To improve this study, I could impose a true dilatational strain (an oscillatory relative volume change) instead of the method used here which is an oscillatory volume change. The nominal strain in this case is equal to the dilatational strain only at low strain values. One type of system this method could also be relevant for is surfactant layers at interfaces, which are inherently more compressible and can exhibit interesting viscoelastic behavior.

References

Johnson, J.K.; Zollweg J.A; Gubbins, K.E.; *The Lennard-Jones equation of state revisited*, **Molecular Physics**, Vol 78, No. 3 591-618