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SHEAR STRESS CORRELATION LENGTH AT CONSTANT PRESSURE

JANKA PETRAVIĆ

Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia[1]

Dedicated to the memory of Professor Vladimir Šips

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Even in simple liquids, shear stress relaxation is a cooperative effect associated with a correlation length. For subsystems of a size smaller than the correlation length, shear stress is determined by the strain at the boundaries. We show that the shear stress correlation length increases with the isobaric decrease in temperature, and quantify this decrease using molecular dynamics simulations of a simple atomic liquid with short-range repulsive interactions in the isothermal-isobaric ensemble with strained periodic boundary conditions.

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1. Introduction

In computer simulations, one is necessarily compelled to consider only finite systems. If a condensed system of particles of finite size is confined between rigid walls, its behaviour is strongly and non-trivially influenced by the interactions with the wall and packing properties. The interest in the relationship between packing properties and confinement in thin films has increased in recent years with the development of nanotechnology [1,2]. However, from the early days of computer simulation, the main purpose has been to reproduce the bulk structural and transport properties in the thermodynamic limit by considering only a finite number of particles. With the aim to eliminate the influence of the boundaries and confinement effects, finite systems are simulated in the Born-von Karman periodic boundary conditions [3]. The underlying idea is that a system in periodic boundary conditions is in fact an infinite system with a peculiar initial state, such that the

[1]Present address: School of Chemistry, The University of Sydney, NSW 2006, Australia
E-mail address: janka@chem.usyd.edu.au

distribution of molecular positions and velocities is spatially periodic. This periodicity is retained forever without constraining the particle motion in any way [4]. System-size effects in the periodic boundary conditions have also been the object of many studies [3, 5 − 7]. Although the number effects are much weaker than in fixed boundaries, their importance increases with the increase in density and the decrease in temperature towards freezing [8].

In a recent paper [9], we have revisited the problem of how specifying some property of the system boundary without restricting particle motion influences the structure of simple liquids, by considering periodic boundaries with finite strain (Fig. 1). We have found that, if the system is smaller than some characteristic size, then arises the shear stress as a consequence of the strain imposed at the boundaries of the periodic cell. In contrast to the shear stress in deformed solids, which is elastic and the result of a change in potential energy under deformation, the shear stress in a small liquid element under strain is of purely entropic origin. It is a consequence of the fact that, in a liquid, a group of molecules cannot rearrange independently of the environment represented by the conditions imposed at its boundaries, unless it has at least some critical size. For smaller systems, the possible rearrangements are such that their ensemble average contains some shear stress related to the boundary strain. The boundary conditions change the angular dependence of the pair distribution function [7] even without strain. With the strain, the resulting asymmetry of the pair-distribution function gives rise to the finite value of the shear stress [10]. At the same time, the transport properties, such as the diffusion coefficient and shear viscosity (computed from the fluctuations with respect to the average shear stress), are not affected, indicating that the number of available configurations, i.e. entropy, is the same in the strained and the unstrained systems [11].

The idea that structural rearrangement requires a coordinated effort of a group of particles is also behind the entropy-based Adam-Gibbs theory of cooperative relaxations close to the glass transition [12]. The Adam-Gibbs theory hypothesizes

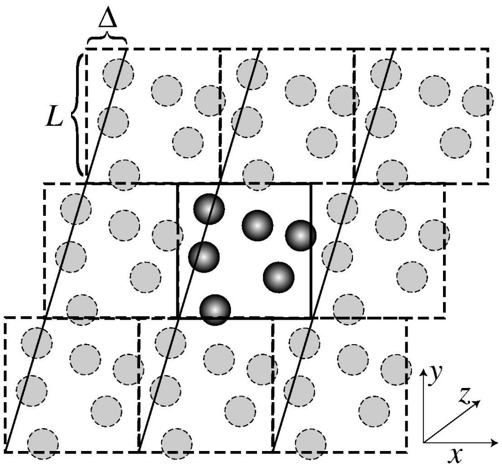


Fig. 1. Strained periodic boundary conditions. Horizontal rows of cubic periodic cells of the side length L are shifted with respect to each other in the x-direction by the distance Δ. This is equivalent to a deformation (tilting) of the periodic cells.

about a characteristic length (the size of a "cooperatively rearranging region") that increases with the isobaric decrease in temperature and diverges at the glass transition.

If we define a group of molecules that can rearrange independently of the environment as a subsystem in which the equilibrium shear stress vanishes irrespective of the boundary conditions, we can regard the minimum side length of a cube containing such a group of molecules as the "shear stress correlation length". In this paper, we show using isothermal-isobaric equilibrium molecular dynamics methods, that this represents a finite characteristic length, increasing with the isobaric decrease in temperature, which exists even in simple liquids above freezing.

2. Simulation method

The model liquid system considered here consists of particles interacting via the short-range Weeks-Chandler-Andersen (WCA) potential [13], i.e. the repulsive part of the Lennard-Jones pair potential, $\Phi_{ij} = 4\epsilon\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right] + \epsilon$ if the distance r_{ij} between the particles i and j is less than $2^{1/6}\sigma$ and zero otherwise, where ϵ is the depth of the Lennard-Jones potential well and σ is the particle exclusion diameter. Lennard-Jones units [3] are used throughout the paper. We use the isothermal-isobaric equilibrium molecular dynamics [14] methods to explore the dependence of the shear stress correlation length on temperature at constant pressure. All simulations were done at the pressure of 17.211, which is the pressure of the WCA periodic system of $N = 256$ particles at the density of $\rho = 1.0$ and the temperature $T = 1.2$ at the strain $\epsilon = 0.0$. The number of particles varied from $N = 108$ to $N = 500$. The isothermal-isobaric Nosé-Hoover equations of motion [14] were integrated using the 5^{th}-order Gear predictor-corrector integrator [3] with the time step of 0.001. The averages of the shear stress were collected in the runs of 10 million time steps for each N for the strains of $\epsilon = 0.0$, 0.125, 0.25, 0.375 and 0.5. The number or size-dependence of the maximum stress was monitored at the temperatures of $T = 1.2$, 1.5 and 2.0.

The strain is introduced using a static version of the Lees-Edwards "sliding brick" periodic boundaries [15] (Fig. 1). The strained system is represented by periodic cells shifted by a distance $0 < \Delta < L$ in the x-direction, where L is the side length of the periodic cell. The dimensionless strain ϵ is the ratio of the shift Δ and L, $\epsilon = \Delta/L$. If the side of the periodic cell is smaller than the shear stress correlation length, the full rearrangement necessary for the complete shear stress relaxation cannot take place within the periodic cell, and the shear stress imposed at the boundaries cannot fully relax [9,10].

Since the system is in an equilibrium isotropic liquid state for all values of strain in the boundary conditions, the time average of all elements of shear stress tensor Π,

$$V\Pi_{\alpha\beta} = \sum_i \frac{p_{\alpha i} p_{\beta i}}{m} + \sum_{i,j>i} F_{\alpha ij} r_{\beta j} - P\delta_{\alpha\beta}\,,$$

should vanish irrespective of the orientation of the reference frame. In Eq. (1), V

is the volume of the simulation cell, α and β are the Cartesian directions, $\boldsymbol{r}_i$ and $\boldsymbol{p}_i$ are the positions and momenta of the particle i, $\boldsymbol{F}_i$ is the total force acting on the particle i, P is the hydrostatic pressure and δ_{ij} is the Kronecker symbol. The shear stress autocorrelation function appears in the Green-Kubo relations for liquid viscosity η [16]

$$\eta = \frac{V}{10k_{\mathrm{B}}T}\int_0^\infty \langle \Pi(0):\Pi(t)\rangle \mathrm{d}t = \frac{V}{10k_{\mathrm{B}}T}\int_0^\infty \sum_{\alpha,\beta=x,y,z} \langle \Pi(0)\Pi(t)\rangle \mathrm{d}t\,, \tag{2}$$

where k_{B} is the Boltzmann constant and the colon denotes double contraction of the second-rank tensor Π. Viscosity (2) of a liquid is finite because the shear stress autocorrelation function decays to zero after a finite relaxation time τ – the liquid cannot support shear stress under strain for a longer time. However, when we calculated the autocorrelation functions in the integrand of the right-hand side of the expression (2) for a small dense liquid system under strain, we found that they did not decay to zero (Fig. 2). This was not a consequence of solidification – we verified that the mean-square displacement had the liquid-like appearance and that there was no cluster formation causing peak splitting in the pair correlation function [9,10].

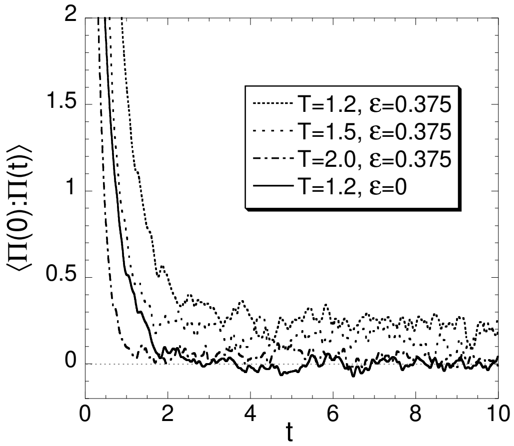


Fig. 2. Shear stress correlation functions of a strained $N = 256$ system at $\epsilon = 0.375$ at three temperatures and at the pressure of 17.211. The correlation function at the lowest temperature and zero strain (full line) is shown for comparison.

The unrelaxed shear stress contained in the finite tail of the correlation function $\langle \Pi(0):\Pi(t)\rangle$ is distributed between the different shear stress elements in a complex way [9]. One way to measure the total shear stress present under strain would be to find the average of the finite tail. However, that would not be practical because it would demand very long simulations. We therefore use a parameter κ defined as the square root of the double contraction of the time-averaged shear stress tensor,

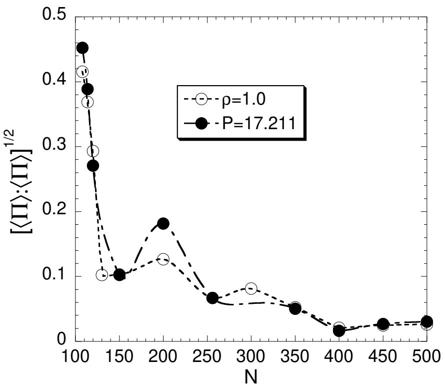
$$\kappa = [\langle \Pi\rangle : \langle \Pi\rangle]^{1/2} = \left[\sum_{\alpha,\beta=x,y,z} \langle \Pi_{\alpha\beta}\rangle\langle \Pi_{\alpha\beta}\rangle\right]^{1/2}, \tag{3}$$

where $\Pi_{\alpha\beta}$ are the Cartesian elements of the shear stress tensor, i.e. the symmetrised traceless stress tensor, and the angle brackets $\langle ...\rangle$ denote the ensemble average. This quantity contains the contributions of all shear stress elements, and is invariant to the reference frame rotation.

The expression (3) is positive definite, but if the average shear stress vanishes, it can be made arbitrarily small in a sufficiently long simulation. We use the average value of κ over different system sizes N in the case when there is no strain ($\epsilon = 0$) as a cutoff in order to decide whether shear stress relaxes or not. Shear stress was considered to have completely relaxed when the highest value of $\kappa(\epsilon)$ was lower than 0.015.

3. *Shear stress correlation length*

Simulation results for the system-size dependence of the maximum value of the shear stress that the system can support under strain at the constant density of $\rho = 1.0$, as measured by the parameter κ, are shown in Fig. 3 (open circles). As observed previously [9,10], for small system sizes shear stress remains finite under strain even if the system remains in the liquid state, and the value of the unrelaxed stress decreases towards zero as the size increases at constant density and temperature. This decrease is not monotonic due to the packing effects. Because for $N \geq 120$, the local minima and maxima follow small variations of hydrostatic pressure in the unstrained system as number of particles is increased at constant density and temperature (Fig. 4, open symbols), it is tempting to speculate that these undulations would disappear if particles are added at constant pressure. However, if



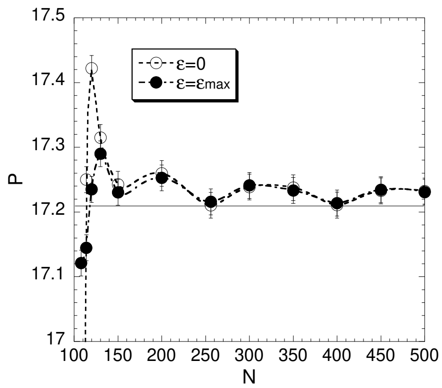


Fig. 3 (left). Dependence of the unrelaxed shear stress (maximum value of the parameter κ over the investigated range of strains) at $T = 1.2$ on the system size at constant density $\rho = 1.0$ (open circles), and at constant pressure $P = 17.211$. The lines connecting the symbols are for eye guidance only. The horizontal dotted line at the bottom of the diagram represents the cutoff value of shear stress.

Fig. 4. Variation of pressure with the system size at constant density $\rho = 1.0$ without strain (open circles) and at the strain $\epsilon_{\max}$ for which the value of κ is maximum (full circles). The lines connecting the symbols are for eye guidance only. The full line represents the pressure of 17.211 used in constant pressure simulations.

we plot the value of the hydrostatic pressure under the strain for which the system can support the largest total shear stress (i.e., for which the value of κ is the largest – full circles in Fig. 4), we see that the hydrostatic pressure is actually lower under strain, which casts doubt on the conjecture. Indeed, straining the system under constant pressure in most cases increases the amplitude of the "damped oscillations" in unrelaxed shear stress (full circles in Fig. 3). The oscillations are most probably due to the complex changes in the angular dependence of the pair-correlation function under strain, which can be predicted by the perturbation-theory analysis analogous to that in Ref. 7.

The effect of isobaric decrease in temperature on the size dependence of the maximum shear stress in a liquid under strain is shown in Fig. 5. Changing temperature at constant pressure has a huge impact on the unrelaxed shear stress at the same system size for small systems. As temperature decreases, a small liquid system can support much a larger shear stress under strain. The size of the system for which shear stress vanishes, irrespective of the strain caused by the boundary effects (or the "shear stress correlation length"), increases with the isobaric decrease in temperature, indicating that the degree of cooperativity increases as the temperature is lowered.

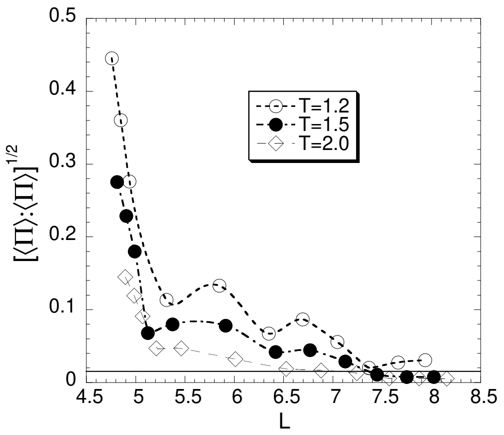


Fig. 5. Variation of the maximum unrelaxed shear stress under strain depending on the system size (the length of the periodic cell) for three temperatures at constant pressure of 17.211.

Shear stress does not relax in a small system with strained periodic boundary conditions because the atomic configurations in a small volume, which can reconcile the requirement that the distribution a boxlegth away is shifted with respect to the original distribution, and at the same time contain no shear stress, are energetically less favourable than those containing some shear stress. In other words, as a consequence of the decrease in configurational entropy (i.e. the number of energetically acceptable configurations) in a small dense system, the nature of the possible packings and the amount of shear stress contained in the system are determined by the configuration at the boundary. Although the simulations of liquid samples with the periodic boundary conditions of any kind are artificial (such systems do not exist in nature), they allow us to study how imposing different boundary conditions on a small subsystem affect its properties, without constraining the particle motion in any direction. Therefore, our result has a physical meaning for bulk liquid systems. In any sufficiently small subsystem with different conditions at boundaries, shear stress will be such as dictated by the boundary conditions and will be correlated over its characteristic length at any instant, although the time average of the shear stress in the subsystem will vanish.

4. *Conclusion*

We have shown that a small dense liquid system in periodic boundary conditions, subjected to constant strain, retains liquid structure, but as in a solid, its shear stress does not completely relax. The fact that small liquid systems can sustain shear stress under constant boundary strain makes them at first sight seem similar to solids. However, shear stress under strain in solids is a result of the change of potential energy in the unique deformed inherent structure, while its origin in liquids is entropic, i.e. a consequence of different probability distributions for shear stress elements.

We showed that the shear stress correlation length can be found by gradually increasing system size until shear stress vanishes for all strains imposed by the periodic boundary conditions. This characteristic length increases with the isobaric decrease in temperature. The shear stress correlation length can be regarded as a measure of the size of an element of liquid over which the shear-stress fluctuations are spatially correlated. In other words, it is an estimate of the size of a region in a liquid that can rearrange independently of environment, which increases with isobaric decrease in temperature. Because of this interpretation, it is tempting to relate it to the size of a "cooperatively rearranging region" of the Adam-Gibbs theory [12] of supercooled liquids. The definitions are indeed similar, and the origins of cooperativity are in both cases in the decrease of the number of accessible configurations. However, the assumptions behind the Adam-Gibbs theory are different and specific to deeply supercooled liquids, with separation of solid-like vibrational modes responsible for most of the excess entropy, and sluggish diffusion during transitions between a few possible inherent structures. The increasing shear stress correlation length studied in this work is specific to an ordinary liquid state; in particular, it is not obvious that it would predict a divergent shear stress relaxation time at some transition temperature. We are currently investigating the behaviour of the shear-stress correlation length in more complex glass-forming liquids and binary mixtures with the approach to the glass transition.

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KORELACIJSKA DULJINA SMIČNOG NAPREZANJA PRI STALNOM TLAKU

U jednostavnim je tekućinama opuštanje smičnog naprezanja skupni učinak povezan s korelacijskom duljinom. U podsustavima koji su manji od korelacijske duljine se smično naprezanje određuje posmicima granica. Pokazujemo da se korelacijska duljina smičnog naprezanja povećava pri izobarnom snižavanju temperature, te određujemo to snižavanje simulacijama molekulske dinamike jednostavne atomalne tekućine s kratko-dosežnim odbojnim međudjelovanjem u izotermičko-izobarnom skupu s posmičnim periodičnim graničnim uvjetima.