

Viscosity, Shear Waves, and Atomic-Level Stress-Stress Correlations

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The Green-Kubo equation relates the macroscopic stress-stress correlation function to a liquid's viscosity. The concept of the atomic-level stresses allows the macroscopic stress-stress correlation function in the equation to be expressed in terms of the space-time correlations among the atomic-level stresses. Molecular dynamics studies show surprisingly long spatial extension of stress-stress correlations and also longitudinal and transverse waves propagating in liquids over ranges which could exceed the system size. The results reveal that the range of propagation of shear waves corresponds to the range of distances relevant for viscosity. Thus our results show that viscosity is a fundamentally nonlocal quantity. We also show that the periodic boundary conditions play a nontrivial role in molecular dynamics simulations, effectively masking the long-range nature of viscosity.

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Computer simulations of supercooled liquids revealed a number of phenomena that happen at a microscopic level. These include atomic caging, stringlike atomic motion, dynamically heterogeneous behavior, and multiple subtle features related to the sampling of potential energy landscape [1]. The nature of the relations between these microscopic phenomena and macroscopic properties, such as viscosity, is not completely understood. Here we address the connection between the local atomic dynamics and macroscopic viscosity by using the concept of the atomic-level stresses [2–8].

One common approach to viscosity calculations in molecular dynamics (MD) simulations is based on the Green-Kubo expression [9–11]:

$$\eta = \frac{V}{k_b T} \int_0^\infty \langle \sigma^{ab}(t_0) \sigma^{ab}(t_0 + t) \rangle dt, \quad a \neq b, \quad (1)$$

where $\langle \dots \rangle$ indicates averaging over the initial time t_0 of the autocorrelation function for off-diagonal components of the macroscopic stress tensor σ^{ab} . The total volume of the system is V , while k_b and T are the Boltzmann constant and temperature, respectively. The macroscopic stress in (1) is a sum of contributions from individual atoms:

$$\sigma^{ab} = \frac{1}{2V} \sum_{i \neq j} \left(\frac{\partial \phi}{\partial r_{ij}} \right) \left(\frac{r_{ij}^a r_{ij}^b}{r_{ij}} \right) = \frac{1}{V} \sum_i s_i^{ab}, \quad (2)$$

where the summation over i is over the all atoms in the system, while the summation over j is over the atoms with which atom i interacts via pair potential ϕ . In (2) we neglected the kinetic energy contribution.

Contributions from individual atoms s_i^{ab} are closely related to the local atomic stresses $\sigma_i^{ab} = s_i^{ab}/V_i$, where V_i is the atomic volume of the atom i [6–8]. Here, for

convenience, we will refer to the parameters s_i^{ab} as the local atomic stress elements.

It follows from (1) and (2) that for a single component system

$$\begin{aligned} (V/\rho_0) \langle \sigma^{ab}(t_0) \sigma^{ab}(t_0 + t) \rangle \\ = \langle s_i^{ab}(t_0) s_i^{ab}(t_0 + t) \rangle + \left\langle s_i^{ab}(t_0) \left\{ \sum_{j \neq i} s_j^{ab}(t_0 + t) \right\} \right\rangle, \quad (3) \end{aligned}$$

where ρ_0 is the atomic number density. The averaging $\langle \dots \rangle$ in (3) and hereafter is over the all atoms i and over the initial time t_0 . The first term on the right is the autocorrelation function for the atomic-level stress elements. The second term contains correlations between atomic-level stress elements on different atoms.

Previously, it was demonstrated that correlation function (3) at zero time extends over large ranges and that the range of distances relevant to viscosity is large [3–5]. Here we demonstrate that propagating stress waves could be observed through this approach and that stress waves play a very important role in formations of viscosity, making it a very nonlocal quantity. We also reveal the nontrivial role of periodic boundary conditions.

In our approach, we define a correlation function (sscf) between the stress element at atom i with the stress elements at a subset of atoms j , which are separated from the atom i by $r \mp \Delta r/2$, as

$$F(r, t) \Delta r \equiv \left\langle s_i^{ab}(t_0) \left\{ \sum_{j \in J_{\Delta r}(i, r, t_0)} s_j^{ab}(t_0 + t) \right\} \right\rangle, \quad (4)$$

where $J_{\Delta r}(i, r, t_0)$ is the set of all atoms that were within the shell of radius r and thickness Δr from the position of atom i at time t_0 . The number of such atoms within a thin shell of

radius r is proportional to $r^2 \Delta r$. The averaging goes over i and t_0 . Note that $F(r=0, t)$ is the autocorrelation function.

Finally, we introduce the concept of microscopic viscosity:

$$\eta(R_{\max}, t_{\max}) \equiv \frac{\rho_o}{k_b T} \sum_{r=0}^{R_{\max}} \int_{t=0}^{t_{\max}} F(r, t) \Delta r dt. \quad (5)$$

This quantity should extrapolate to the macroscopic viscosity in the limits of $R_{\max} \rightarrow \infty$ and $t \rightarrow \infty$ and thus address the ranges of correlations in space and time that affect viscosity.

To examine the behavior of the microscopic viscosity and its convergence to the macroscopic value, MD simulations were performed on a single component system of particles that is supposed to mimic liquid iron. The number density of the system corresponded to a bcc lattice with lattice spacing $a = 2.943 \text{ \AA}$. The particles interact through a short-range pairwise potential. The potential has a minimum at 2.61 \AA with the depth $\approx 2800 \text{ K}$, and it is zero beyond 3.44 \AA . This potential is more harmonic than the Lennard-Jones potential, but these potentials share very similar thermal behaviors of atomic-level stresses at high temperatures [8]. Thus we surmise that results obtained by using this potential are rather general. The melting temperature of this system is around 2400 K , while the glass transition temperature is around 1000 K [12].

In calculating (3) for every atom i , every atom j should be counted only once. For instance, if the simulations are performed on a cubic system ($L \times L \times L$) with periodic boundary conditions and if the radius of the shell r in (4) belongs to the interval $(L/2) < r < \sqrt{3}(L/2)$, according to (3), we should count only the atoms in parts of the shell under the ‘‘corners’’ of the cube. Thus, we should count every atom j only once without introducing extra images of the system. Consequently, sscf (4) approaches zero as r approaches $\sqrt{3}(L/2)$ since the number of atoms j that we should count goes to zero. Thus, size effects in sscf may appear if it does not decay quickly with an increase of r .

In order to assess the size effects, we studied cubic systems containing 1458, 5488, and 43 904 particles (small, intermediate, and large, respectively) with periodic boundary conditions. The half lengths of their sizes, $(L/2)$, are $\sim 13.25 \text{ \AA}$, $\sim 20.60 \text{ \AA}$, and $\sim 41.21 \text{ \AA}$, respectively.

In order to evaluate macroscopic viscosity we integrated total shear stress correlation functions according to (1) for the systems of different sizes up to the time $t_{\max} = 2000 \text{ (fs)}$, where stress correlations decay to zero. Results from different stress components and from several runs were used to find the average values and the errors. The obtained values of the macroscopic viscosities for different systems at 2000 (K) are $\eta(13.25 \text{ \AA}) = 0.01084 \pm 0.00012 [\text{kg}/(\text{s} \cdot \text{m})]$, $\eta(20.60 \text{ \AA}) = 0.01055 \pm 0.00017 [\text{kg}/(\text{s} \cdot \text{m})]$, and $\eta(41.21 \text{ \AA}) = 0.01097 \pm 0.00115 [\text{kg}/(\text{s} \cdot \text{m})]$. Thus the values for macroscopic viscosities for all systems are very similar. Our results are

consistent with other reports [9,11] suggesting the absence of significant size effects in viscosity calculations. The similarities in values of macroscopic viscosities obtained on systems of different sizes may appear to suggest that viscosity is a relatively local quantity. However, some previous results indicate that viscosity is, in fact, very nonlocal [3,13]. Here we further address this issue.

Figure 1 shows the 2D plots of sscf (4) at temperature 2000 K for the small and large systems. There were six independent runs to produce the data for the system containing 43 904 particles. In every run the averaging was done over every atom in 230 initial structures separated from each other by 100 fs . This corresponds to averaging over more than 60×10^6 central atoms. Averaging over different stress components was also employed. The value of the stress autocorrelation function at time zero is $5.5 \text{ (eV}^2)$. Overall, the value of the signal that we observe at large r is rather small compare to the size of fluctuations. For the large system we stopped calculations at 30 \AA because calculations consume significant computer time and memory for large distances. However, for the smaller

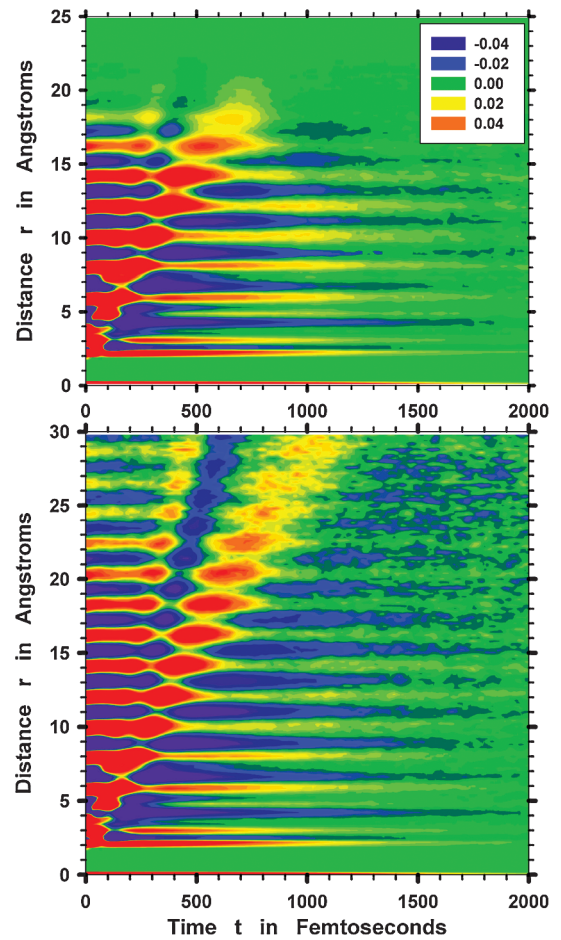


FIG. 1 (color). The stress-stress correlation function $F(r, t)$ [Eq. (4)] at 2000 K for $(L/2) = 13.25 \text{ \AA}$ (upper panel) and $(L/2) = 41.21 \text{ \AA}$ (lower panel), $\Delta r = 0.2 \text{ \AA}$. The color corresponds to the amplitude of sscf function.

systems calculations are less time-consuming, and we performed calculations up to the distances where all particles were included.

Figure 1 demonstrates that spatial ranges of stress correlations extend beyond 10 interatomic distances in agreement with Ref. [13]. The interchanging horizontal regions of positive and negative intensity should be related to the oscillatory behavior of the pair density function. Two bright lines with slopes corresponding to ≈ 6 km/s and ≈ 3 km/s should be caused by longitudinal and transverse stress waves. The stress waves propagate in the large system beyond 30 Å but disappear in the small system around 20 Å. Thus periodic boundary conditions affect propagation of stress waves. It follows from Fig. 1 that every atom in the system is a source of stress waves at every instant. Since stress waves propagate over significant distances, it follows that stress waves from different atoms can propagate through each other. It also means that the stress on every atom is affected by all the stress waves that pass or passed through the atom.

Further we address the connection between the sscf and viscosity. Figure 2 shows how the microscopic viscosity $\eta(R_{\max}, t_{\max})$ depends on R_{\max} for a few different integral cutoffs t_{\max} for the systems of three different sizes. Figures 2(a)–2(e) present results for 2000 (K) while Fig. 2(f) for 10 000 (K). The value of the microscopic viscosity at $R_{\max} = 0$ is associated with the stress autocorrelation function ($j = i$). Then the value increases with the inclusion of the first coordination shell. Figures 2(a)–2(e) show the evolution of the sscf with t_{\max} . It follows from the figure that contributions to viscosity from autocorrelation and cross terms in (3) are comparable for all t_{\max} . Note that for every t_{\max} the range of distances relevant for viscosity corresponds to the range that shear wave propagate in that time. Comparison with Fig. 1 reveals that, for the large system and times less than 800 (fs), crossing of the front of the shear stress wave has major effects on microscopic viscosity, while changes are slow and small before and after the wave. Longitudinal wave also does not seem to affect microscopic viscosity.

Figures 2(c)–2(e) show explicitly that viscosity is a very nonlocal quantity. It would be local if the size-independent behavior presented in Figs. 2(a) and 2(b) for small cutoff times would hold for all cutoff times. However, the results show distinct size effects on the microscopic viscosity. For the large times, the fronts of the shear waves cannot be crossed because of the insufficient sizes of the systems. Thus, microscopic viscosity starts to increase at some other distance. As the number of included atoms j approaches the total number of atoms in the system, the microscopic viscosity saturates to the values of the macroscopic viscosities. For the large system, this corresponds to the centers of the green bands in Figs. 2(e) and 2(f). The widths of the green bands give the standard deviations of the macroscopic value σ .

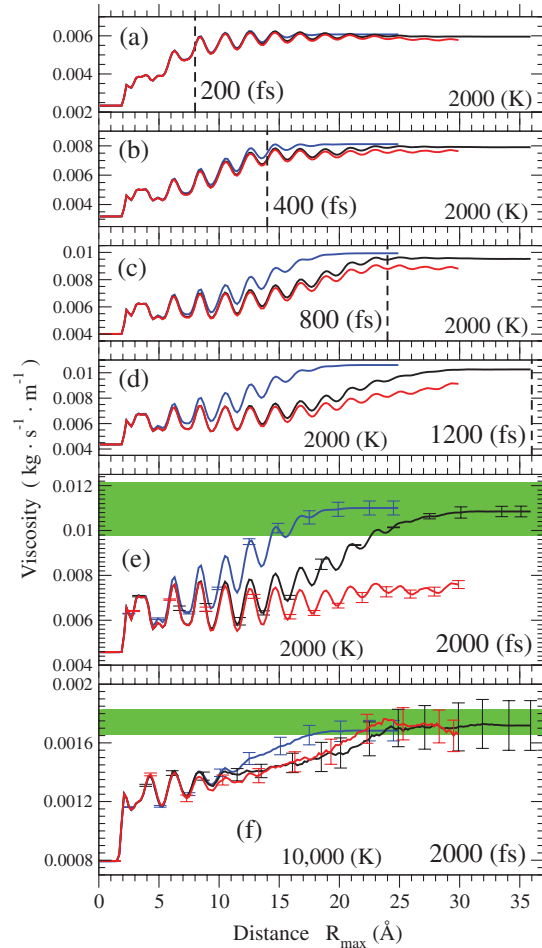


FIG. 2 (color). Microscopic viscosities for the systems of different sizes as a function of R_{\max} for some values of t_{\max} . (a)–(e) are for 2000 (K), while (f) is for 10 000 (K). The vertical dashed lines in (a)–(c) mark the range that shear wave propagate in that time. The blue, black, and red curves show results for the small, intermediate, and large systems, correspondingly. The middle of the green bands in the 2000 (fs) panels represents the values of the macroscopic viscosities for the large system. Their widths give the errors.

For the small and intermediate size systems, the saturated values of microscopic viscosities are very close to the corresponding macroscopic values and to the values of the macroscopic viscosities for the large system. By definition, the microscopic viscosity for the largest system also should saturate to the value of the macroscopic viscosity as all particles become included.

The present results expose a puzzle, i.e., why macroscopic viscosities are similar while microscopic viscosities show size dependence. A solution may lie in the nature of stresses, stress waves, and periodic boundary conditions. Consider the wave that starts from the atom i and that would reach the atom j' at time t in an infinite system. Because of the periodic boundary conditions, this wave reaches the atom j inside the box instead, as shown in Fig. 3. Let us assume that different stress waves contribute

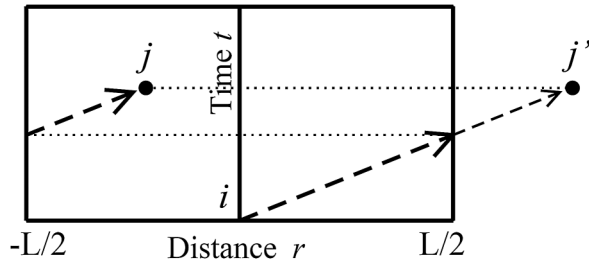


FIG. 3. The periodic boundary conditions effectively return stress waves that leave the box back into the box.

additively to the stresses on the atoms. Then periodic boundary conditions effectively transfer contributions of the wave to the stresses from j' onto j . Thus, the wave that arrives at the atom j has the same effect on the macroscopic stress correlation function (3) as would the wave that would arrive at j' in an infinite system. Thus the macroscopic stress correlation function and correspondingly macroscopic viscosities obtained on any finite size system may appear to be similar to the results that could be obtained on an infinite size system.

Thus, in our view, the long-range nature of viscosity is obscured by the nontrivial role that periodic boundary conditions play in MD simulations. The apparent lack of size effect in the macroscopic viscosity does not indicate the local nature of viscosity, and in reality viscosity is a highly nonlocal quantity.

In view of our conclusion on the nonlocal nature of viscosity, it is interesting to estimate the range of distances which are relevant for viscosity. This estimate could be obtained if the results for the microscopic as well as macroscopic viscosities on systems of different sizes become the same. Figure 2(f) shows the results at 10 000 K. Here the results for the intermediate and large systems agree, not only in the saturation value but in the entire dependence on R_{\max} . Only the small system shows the size effect due to the boundaries. Thus at this temperature both the macroscopic viscosity shown by the green stripe and the microscopic viscosities become independent of size for systems with L larger than 20 Å, a surprisingly long range for such a high temperature.

Thus, one can expect that in the liquid at low temperature the range of distances relevant for viscosity is even longer. Such a long correlation length and the nonlocal nature of viscosity is indeed consistent with the literature [2–5,9–11,13–19]. Here, however, we revealed a number of details which, in our view, were not discussed previously and are important.

In summary, we studied the microscopic nature of viscosity in a liquid. Our results demonstrate that viscosity is a fundamentally nonlocal quantity and illustrate how the propagation of stress waves is related to formation of viscosity. Our results also show that periodic boundary conditions play a rather nontrivial role in MD simulations. The results raise multiple questions concerning the nature of viscosity and stress wave propagation in liquids.

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