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# Viscoelasticity of glycerol at ultra-high frequencies investigated via molecular dynamics simulations

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We present a calculation of the shear and longitudinal moduli of glycerol in the gigahertz frequency regime and temperature range between 273 K and 323 K using classical molecular dynamics simulations. The full frequency spectra of shear and longitudinal moduli of glycerol between 0.5 GHz and 100 GHz at room temperature are computed, which was not previously available from experiments or simulations. We also demonstrate that the temperature dependence of the real parts of the shear and longitudinal moduli agrees well with available experimental counterparts obtained via time-domain Brillouin scattering. This work provides new insights into the response of molecular liquids to ultra-high frequency excitation and opens a new pathway for studying simple liquids at high frequencies and strain rates. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4940146>]

## I. INTRODUCTION

The viscoelastic behavior of simple Newtonian liquids, such as water and glycerol, was shown recently to exert a strong effect on nanomechanical systems operating in the gigahertz (GHz) frequency regime.<sup>1</sup> While all liquids support shear at frequencies greater than their relaxation rate, it is a challenge to experimentally quantify the viscoelasticity of simple liquids, such as glycerol at ambient temperature, which exhibit average relaxation times in the nanosecond range. There are well-established experimental techniques to characterize longitudinal deformations in liquids,<sup>2</sup> but techniques that probe liquid response under shear in the gigahertz regime (ultra-high frequencies) are sparse<sup>3–5</sup> — due to the short time and length scales associated with molecular/atomic motion that are difficult to directly capture with conventional methods such as dynamical mechanical analysis (DMA) or ultrasonics.

Characterizing the short time scale relaxations and high rate deformations of liquids is also essential for a number of other important areas including mechanical stress relaxation processes in glass-forming liquids<sup>6</sup> such as those investigated via ultrasonic<sup>7,8</sup> and newly developed time-domain Brillouin scattering (TDBS)<sup>3–5</sup> techniques. Viscoelastic response of liquid films confined to molecular dimensions and subjected to high frequency oscillatory deformations is important in understanding nanotribological behavior.<sup>9–12</sup> Rapid high strain deformations and viscoelastic response are also responsible for energy localization during mechanical insults at the interfaces in multiphase materials such as energetic materials<sup>13</sup> with important consequences for processes such as energetic material initiation.

Classical molecular dynamics (MD) simulations are extensively used to probe the viscoelastic behavior of

many complex systems, including glass-forming liquids and polymers (see, e.g., Refs. 14 and 15). Advances in the development of accurate force fields and the availability of high performance computing allow the use of MD to obtain both qualitative and quantitative predictions for a variety of properties, including mechanical moduli. There is limited availability of experimental data for the mechanical response of simple liquids in the gigahertz frequency range, but knowledge of liquid viscoelasticity in this regime holds significant implications for fundamental models of liquid behavior and applications such as vibrating nanostructures immersed in liquids.<sup>1</sup> Therefore, we use MD simulations to determine the real (storage) and imaginary (loss) components of the shear and longitudinal moduli of glycerol — a prototypical viscous simple liquid — at frequencies from 0.5 GHz to 100 GHz. We leverage the ability of MD to probe molecular processes on tenths of nanoseconds as required for exploring material properties at these frequencies.

## II. GLYCEROL MODEL AND SIMULATIONS DETAILS

We choose the glycerol model of Chelli<sup>16,17</sup> and Blicek,<sup>18</sup> which is based on AMBER-FF<sup>19</sup> and is known to well reproduce glycerol transport properties (see, e.g., Ref. 20) and the coherent intermediate scattering function (see, e.g., Ref. 21) obtained from neutron scattering experiments. See supplementary material in Ref. 22 for additional model and simulation details.

All simulations are performed on bulk glycerol with an ensemble of 2744 molecules under constant temperature and volume conditions using LAMMPS software.<sup>23</sup> We consider a monoclinic (non-orthogonal) simulation box. We apply periodic boundary conditions in all three dimensions and perform time-periodic, spatially uniform strain deformations in the NVT ensemble. See supplementary material in Ref. 22 for configuration preparation procedures.

These simulations contrast to those commonly reported. They are not non-equilibrium molecular dynamics (NEMD)

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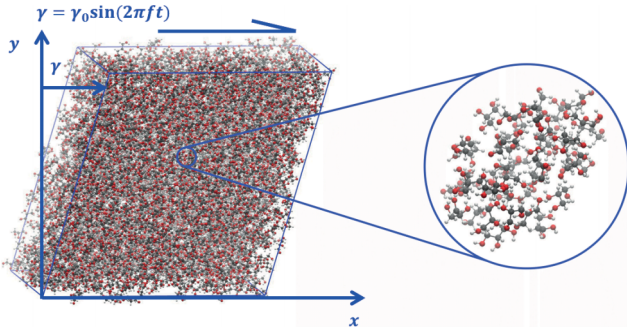


FIG. 1. Shear deformation of a MD simulation cell and enlarged region with glycerol molecules taken from the center of the cell. Periodic boundary conditions are applied in all three dimensions to ensure the system is free of surface effects. For visualization purposes,  $\gamma_0$  in the figure is substantially larger compared to  $\gamma_0$  in the actual simulations.

simulations that are generally used to investigate the strain-rate dependence of viscosity (which is not our intention) in molecular fluids — the presented approach does not offer an alternative to NEMD. Furthermore, we do not deal with liquids experiencing continuous flow induced by either an externally imposed velocity field or a moving boundary at the surface. Our approach is based on strain deformations commonly employed in exploring materials showing an elastic component in their mechanical response<sup>24</sup> and is analogous to the loading commonly applied in DMA experiments to measure viscoelastic material response. To compute shear and longitudinal moduli, we, respectively, apply a periodic shear strain,  $\gamma(t) = \gamma_0 \sin(2\pi ft)$ , and longitudinal strain,  $\epsilon(t) = \epsilon_0 \sin(2\pi ft)$ , with a constant maximum strain rate on a three dimensional cubic box. Here,  $f$  is the frequency of oscillation (Hz) and  $\gamma_0$  and  $\epsilon_0$  are the amplitude of shear and longitudinal deformations, respectively. A schematic of the shear deformation of the entire 3D cubic box, and an enlarged region with glycerol molecules, is shown in Figure 1.

The resulting 6-component stress tensor is computed as

$$\sigma_{IJ}(t) = \left( \frac{\sum_k^N m_k v_{kI} v_{kJ}}{V} + \frac{\sum_k^N r_{kI} F_{kJ}}{V} \right),$$

where  $N$  is the number of atoms in the system;  $I$  and  $J$  are indices representing any of the Cartesian coordinates  $x, y, z$ ;  $V$  is the volume of the system;  $m$  is the atomic mass;  $v$  is the atom's velocity;  $r$  is the atom's position; and  $F$  is a sum of all forces on each atom. We calculate and store  $\sigma_{IJ}(t)$  every 10 ps during a simulation for post-processing.

The periodic shear deformation,  $\gamma = \gamma_0 \sin(2\pi ft)$ , is applied in the  $x$ -direction (see Figure 1), and we analyze the resulting stress tensor component  $\sigma_{xy}(t)$ . For a linear viscoelastic system,  $\sigma_{xy}(t)$  is also a periodic function of time, and given by  $\sigma_{xy}(t) = \sigma_0 \sin(2\pi ft + \delta_S)$ , where  $\sigma_0$  is the magnitude of the shear stress,  $f$  is the frequency of oscillation (that is imposed), and  $\delta_S$  is the phase difference between stress and strain.  $\sigma_0$  and  $\delta_S$  are calculated by performing a Discrete Fourier Transformation (DFT) on the  $\sigma_{xy}(t)$  time series. The real and imaginary parts of the shear modulus,  $G$ , are given by  $G' = \frac{\sigma_0}{\gamma_0} \cos \delta_S$  and  $G'' = \frac{\sigma_0}{\gamma_0} \sin \delta_S$ , respectively. The longitudinal modulus,  $M$ , is calculated in a similar

manner. It is important to impose sufficiently small-amplitude oscillatory shear so that the liquid structure and consequent stress relaxation processes due to atomic rearrangements are not affected by the deformation. In our reported simulations,  $\gamma_0 = \frac{d}{L} = 0.005$  is chosen (after systematic refinement), where  $d$  is the displacement and  $L = V^{\frac{1}{3}}$  is the length of the simulation box. See supplementary material in Ref. 22 for additional data analysis procedures.

The aforementioned methodology is directly analogous to classical DMA of macroscopic solids, which is widely used to experimentally study the viscoelastic properties of materials, for frequencies up to hundreds of megahertz. DMA is not experimentally accessible in the gigahertz frequency range due to the limited frequency response of available mechanical transducers. This straightforward approach has not been applied before, to our knowledge, in the context of simple liquids. It is also uniquely well suited to probe elastic response of simple liquids and allows a simple method to directly access the short time scale molecular scale relaxations that dominate behavior in this regime.

### III. RESULTS

Figure 2 shows the temperature dependence of the real and imaginary components of (a) the shear moduli,  $G'$  and  $G''$ , at  $f = 25$  GHz and (b) the longitudinal moduli,  $M'$  and  $M''$ , at  $f = 41.5$  GHz. For comparison, we also show experimental measurements of  $G'$  and  $M'$  reported in Ref. 5. Both storage moduli  $G'$  and  $M'$  decrease as temperature increases, as expected. The simulated temperature trends of  $G'$  and  $M'$  are in excellent agreement with experimental measurements.  $G''$  and  $M''$  increase slightly as temperature increases; no experimental data for the loss moduli are available for comparison.

The computed  $G'$  and  $M'$  values at these frequencies are 20%-25% lower than measured values in Ref. 5. A portion of this discrepancy may be due to the simulated density being lower than the experimentally measured densities. Higher values for  $G'$  and  $M'$  close to experiment can be recovered from the MD simulations, with relatively small (but artificial) changes in the simulated density. This discrepancy is likely due to the simulated density being lower than the experimentally measured densities. Experimental values for  $G'$  and  $M'$  could be recovered from the MD simulations, with relatively small (but artificial) changes in the simulated density.

We also find that a generalized Cauchy relationship (gCR)<sup>5,25</sup> ( $M' = A + BG'$ ) holds remarkably well for our data and yields the relationship,  $M' = 4.5 + 2.98G'$ , in the temperature regime studied; see Figure S4 of the supplementary material in Ref. 22 for comparison between the gCR obtained via simulation and experiment. Here,  $A$  is material dependent constant with weak temperature dependence and  $B$  is always close to 3. The standard error for the intercept and slope is 0.1 and 0.06, respectively. Remarkably, the intercept  $A = 4.5$  GPa is in excellent agreement with intercept values reported in the literature,<sup>26,27</sup>  $A = 4.61 \pm 0.85$ , obtained from experiments at much lower frequencies.

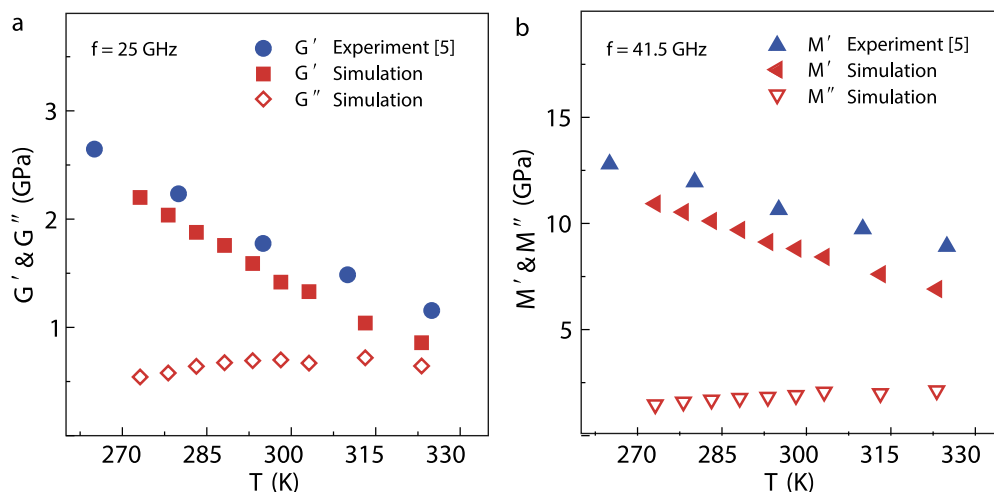


FIG. 2. Glycerol viscoelastic data versus temperature. (a) Temperature dependence of MD simulated real,  $G'$  (open squares), and imaginary,  $G''$  (open diamonds), components of the shear modulus of glycerol, at frequency  $f = 25$  GHz and (b) temperature dependence of real,  $M'$  (open left triangles), and imaginary components,  $M''$  (open down triangles) of the corresponding longitudinal modulus, at frequency  $f = 41.5$  GHz. These frequencies are chosen to match available measurements. Error bars in  $G$  and  $M$  for the simulations, representing one standard deviation based on 5 samples, are comparable to the symbol size (not shown for clarity). Time-domain Brillouin scattering (TDBS) measurements for  $G'$  (open circles) and  $M'$  (open up triangles) at the same frequencies from Ref. 5 are shown for comparison.

It is well established that gCR holds for a broad range of isotropic materials, including metallic glasses, ceramics, epoxies, and molecular liquids at lower frequencies.<sup>26,28</sup> This universality is somewhat unexpected and not well-understood due to the structural, dynamical, and chemical differences and complexity of these materials. One possible explanation for these observations is that at such high frequencies, molecules act as individual particles so the influence of molecular topology (intermolecular degrees of freedom) on elasticity is small. The dominant interactions that drive elastic behavior would then appear to be repulsive central force interactions (in this case Coulombic and van der Waals). This could have significant implications for MD simulations of complex liquids at high frequencies, suggesting the ability to use

coarse-grained models to capture the elastic response of these systems with only central body interactions.

Figure 3 shows the angular frequency dependence of the storage (real) and loss (imaginary) shear moduli,  $G'$  and  $G''$ , and longitudinal moduli,  $M'$  and  $M''$ , at  $T = 298$  K. Both  $G'$  and  $M'$  steadily increase from 0.5 GHz to approximately 40–50 GHz and appear to plateau at higher frequencies. A similar trend is observed in  $M'$  for a comparable frequency range [see Figure 3(b)], based on data from Ref. 5. The plateau and sub-linear frequency dependence in  $G'$  observed here for glycerol ( $G'(\omega) \sim \omega^\beta$ , where  $0 < \beta < 0.3$ ) is similar to that seen in soft glassy materials (SGMs) such as emulsions and suspensions.<sup>29</sup> The plateau in  $G'$  in suspensions is attributed to the system approaching a glass transition.<sup>30</sup>

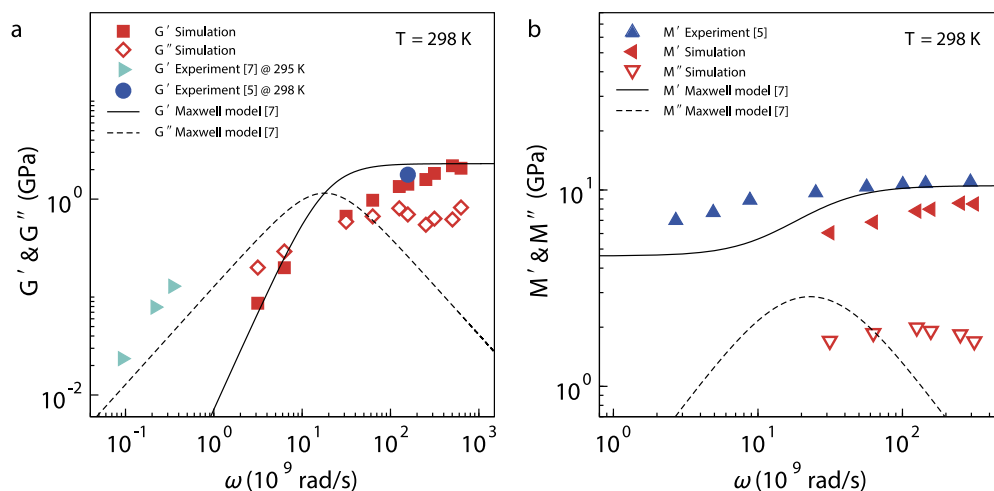


FIG. 3. Glycerol viscoelastic data versus angular frequency,  $\omega = 2\pi f$ . (a) Angular frequency dependence of the real,  $G'$  (solid squares), and imaginary,  $G''$  (open diamonds), components of the shear modulus of glycerol and (b) frequency dependence of the corresponding real,  $M'$  (solid left triangles), and imaginary,  $M''$  (open down triangles), components of the longitudinal modulus, both at  $T = 298$  K. Error bars in  $G$  and  $M$  for the simulations, representing one standard deviation obtained from 5 samples, are smaller than the symbol size (not shown for clarity). Experimentally measured  $G'$  at lower frequencies are shown for comparison in (a). Experimentally measured  $M'$  over a similar frequency range and at a comparable temperature are shown for comparison in (b). Linear Maxwell model predictions for  $G$  and  $M$  computed from data in Ref. 7 are shown in (a) and (b), respectively.



Here, the plateau in  $G'$  and  $M'$  could suggest that the glycerol molecules are frozen and there is no possibility for configurational rearrangement at these ultra-high frequencies.  $G''$  and  $M''$  remain nearly constant between 5 GHz and 100 GHz, indicating solid-like behavior. To our knowledge, these represent the first report of  $G'$  and  $G''$  for glycerol in the frequency range between 0.5 GHz and 100 GHz at  $T = 298$  K.

Observed trends for ultra-high frequency dynamic shear and longitudinal moduli, shown in Figure 3, do not follow the predictions of a linear Maxwell model that is frequently used to describe viscoelastic response of similar materials. Dynamic moduli in Figure 3 can be well-represented with a generalized Maxwell model with five terms corresponding to five different relaxation times (not shown). Multiple relaxation times may indicate mechanisms involving coordination of many molecules. Existence of multiple relaxation times is found in systems approaching glass transition<sup>31</sup> and attributed to emergence of cooperative relaxations and dynamical heterogeneities.<sup>32</sup> It is also found in dilute polymer solutions and attributed to modes of coordinated segmental motion of the polymer.<sup>33</sup>

This indicates the need to develop improved viscoelastic models that are able to capture multiple relaxation modes and cooperative relaxations present at ultra-high frequencies, perhaps in analogy to theoretical approaches developed to capture cooperative motion in glass-forming systems (e.g., Refs. 34–39) and polymer solutions (e.g., Refs. 30, 40, and 41). Development of more accurate viscoelastic models would significantly improve predictions of mechanical behavior in systems whose dynamics lie in this frequency range, such as nanoresonators immersed in liquid.<sup>42</sup>

#### IV. CONCLUSIONS

The broader significance of our results includes the following: (1) Demonstration of the capability of MD as an effective tool for predicting the viscoelastic properties of simple liquids at ultra-high frequencies. This is shown by the excellent agreement between the simulated and experimentally measured temperature dependence of  $G'$  and  $M'$ . (2) Extension of the DMA approach to the GHz frequency regime using classical MD simulations. (3) Computation of the mechanical frequency spectra of a prototypical viscous simple liquid, glycerol, in a frequency range not yet accessed by experiments. (4) Proposition of a simple methodology to study the viscoelastic properties of all simple liquids in the gigahertz (and higher frequency) regime. (5) Demonstration of the applicability of a generalized Cauchy relationship for a simple molecular liquid at high frequencies, indicating the dominance of central forces. (6) The emergence of a plateau in  $G'$  and  $M'$ , suggesting glycerol may experience structural arrest similar to systems approaching a glass transition.

This study opens pathways to theoretical design for nanomechanical device operation in a variety of simple liquids. Such a capability was not previously available, requiring measurement to quantify the liquid's natural viscoelastic response. This new capability enables assessment

of mechanical device operation prior to fabrication, and the use of the non-Newtonian behavior of simple liquids to accentuate the sensitivity of their operation, e.g., due to mass adsorption. Indeed, it was recently demonstrated<sup>1,42</sup> that the quality factors of mechanical resonators (metallic nanostructures) are dramatically enhanced (by orders of magnitude) by the natural viscoelastic response of simple liquids. This unlocks the possibility of achieving molecular scale mass detection in liquid using ultra-small mechanical sensors, with potential applications in targeted medicine and drug delivery.

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