

Microscopic Origin of Shear Relaxation in a Model Viscoelastic Liquid

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An atomistic description of shear stress relaxation in a viscoelastic liquid is developed from first principles through accurate molecular dynamic simulations in a model Yukawa system. It is shown that the relaxation time τ_M^{ex} of the excess part of the shear stress autocorrelation function provides a correct measure of the relaxation process. Below a certain critical value Γ_c of the Coulomb coupling strength, the lifetime of local atomic connectivity τ_{LC} converges to τ_M^{ex} and is the microscopic origin of the relaxation. At $\Gamma \gg \Gamma_c$, i.e., in the potential energy dominated regime, $\tau_M^{\text{ex}} \rightarrow \tau_M$ (the Maxwell relaxation time) and can, therefore, fully account for the elastic or “solidlike” behavior. Our results can help provide a better fundamental understanding of viscoelastic behavior in a variety of strongly coupled systems such as dusty plasmas, colloids, and non-Newtonian fluids.

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It is generally accepted that all liquids are viscoelastic in nature, meaning that their mechanical response to an external force will be both viscous and elastic at the same time. This can be explained through the concept of the Maxwell shear relaxation time scale τ_M such that at times $t \ll \tau_M$, the response of the liquid will be dominantly elastic, and at $t \gg \tau_M$, the response will be dominantly viscous. At intermediate time scales, both elastic and viscous features will be comparable. The stresses endured by such liquids may depend significantly upon their deformation history, thus, leading them to exhibit strain rate-dependent viscosity or “non-Newtonian behavior.” Viscoelasticity is seen in a wide variety of systems ranging from high-performance engineering materials [1], colloidal suspensions [2], and laboratory dusty plasmas [3] to even in rheology of blood flows [4]. This makes viscoelastic systems a subject matter of great interest and sets up a pressing need to develop atomistic theories that will serve as a bridge to connect the macroscopic bulk mechanical response to the underlying microscopic dynamics. In this Letter, we report on such an atomistic study to delineate the microscopic origins of viscoelastic behavior in a model Yukawa liquid.

The Yukawa liquid provides an excellent model for a wide variety of strongly coupled systems such as laboratory and astrophysical dusty plasma systems, charged colloids, and liquid metals [5,6]. The particle interaction potential used in this liquid has the form $\phi(r) = (Q^2/4\pi\epsilon_0 r) e^{-r/\lambda_D}$ where Q and λ_D refer to the particle charge and Debye shielding distance, respectively. The thermodynamic state point of the Yukawa liquid is completely characterized by two dimensionless quantities, namely, the screening parameter $\kappa = a/\lambda_D$ and the coupling strength $\Gamma = Q^2/4\pi\epsilon_0 a k_B T$. Here, a is the Wigner-Seitz radius such that $\pi a^2 n = 1$, with n being the areal number density. In a strongly coupled Yukawa liquid (SCYL), the average Coulomb interaction

energy can exceed the average kinetic energy per particle, thus, leading to $\Gamma > 1$. A direct consequence of this is the emergence of solidlike features such as sustaining low-frequency shear modes [7] originally predicted in theoretical works [8,9] and later realized in laboratory experiments [10]. This makes SCYL a good model system to study a range of collective phenomena in strongly coupled systems. SCYLs have also been shown to be excellent test beds for modeling hydrodynamic flows [11–13], self-organization phenomena such as clustering [14], and lane formation [15] in complex plasmas. A significant amount of numerical work has also been done on the viscosity measurements in SCYL using both equilibrium [16–18] and nonequilibrium molecular dynamics simulations [19,20]. These studies have confirmed the existence of a viscosity minimum at some crossover value $\Gamma_c(\kappa)$ arising due to the competition between the ideal and excess part of the stress tensor. In later works, viscoelasticity was also quantified using both experiments [3,21] and numerical simulations [22] where the crossover frequency for the real and imaginary parts of the complex viscosity was shown to be empirically related to the inverse Maxwell time. It was shown in Ref. [22] that this crossover frequency develops a maximum at some $\Gamma_c(\kappa)$, implying a minimum in the Maxwell time τ_M at the same $\Gamma_c(\kappa)$. However, a systematic study of the microscopic origin of shear relaxation and Maxwell time in these liquids at various (Γ, κ) values is still lacking.

The aim of this Letter is to fill this gap and to provide from first principles, an atomistic picture that would provide answers to the following two fundamentally important questions: (i) What is the connection between the microscopic world and the macroscopic shear relaxation in these SCYL systems? (ii) Is τ_M the correct representation of the duration of dominant elastic response for these liquids, especially at $\Gamma < \Gamma_c(\kappa)$? To address the first question, we have calculated the lifetime of local

atomic connectivity τ_{LC} [23] and found that it converges to the relaxation time τ_M^{ex} of the excess part of the shear stress autocorrelation function for $\Gamma < \Gamma_c(\kappa)$. Since τ_{LC} corresponds to the time duration during which the topology of nearest neighbors remains intact, the fact that $\tau_M^{\text{ex}} \rightarrow \tau_{LC}$ for $\Gamma < \Gamma_c(\kappa)$ directly indicates that τ_M^{ex} is the correct measure of the duration of dominant elastic response at these temperatures and not τ_M . This is markedly different from the behavior observed in ordinary liquids, where, as reported in Ref. [23], τ_{LC} converges to τ_M below the crossover temperature. It is important to note that none of those ordinary liquids show a nonmonotonic behavior in τ_M with temperature. We also show that at $\Gamma > \Gamma_c(\kappa)$, τ_{LC} deviates from τ_M^{ex} directly indicating a crossover from a kinetic regime to a potential energy dominated regime. It should be noted that the shear relaxation time τ_M reported in our work only refers to a measure of the duration of the autocorrelation of shear stress and does not assume an exponential relaxation of the memory function, which was recently questioned in Ref. [24]. Our study further shows that the infinite frequency shear modulus G_∞ does not have a minimum at any temperature, as opposed to the viscosity data which have a well known minimum at $\Gamma = \Gamma_c(\kappa)$. In the following, we provide the details of our numerical work and also explain the procedure used to extract quality data.

Numerical simulations.—We have performed molecular dynamics (MD) simulations on a two-dimensional (2D) Yukawa liquid in a canonical ensemble under periodic boundary conditions. All distances are normalized to Wigner-Seitz radius a , the energies are normalized to $Q^2/4\pi\epsilon_0 a$, and times are normalized to ω_{pd}^{-1} . Here ω_{pd} is the 2D nominal plasma frequency given by $\omega_{\text{pd}} = (Q^2/2\pi\epsilon_0 m a^3)^{1/2}$. The simulation box contains 5016 particles at a reduced number density $n = \pi^{-1}$. The dimensions of the rectangular box were chosen to be $125.705\,291 \times 125.358\,517$, which allows for the formation of a perfect triangular lattice below the freezing transition. The interaction potential is truncated smoothly to zero along with its first two derivatives by employing a fifth-order polynomial as a switching function in the range ($r_m < r < r_c$), where r_m and r_c are the inner and the outer cutoff, respectively. We chose r_m and r_c subject to the criteria $\phi(r_m) \approx 2.27 \times 10^{-6}$ and $\phi(r_c) \approx 1.49 \times 10^{-7}$, thus, ensuring negligible perturbation to the bare Yukawa potential. A Nose-Hoover thermostat [25] with a time constant of $1/\sqrt{2}$ is employed to maintain the temperature at a desired Γ . To improve statistics, we have averaged our data over an ensemble of 4000 independent realizations. This was necessary to reduce the fluctuations present in the long time tail of the stress relaxation function originating from the long-range nature of the interaction potential.

The stress relaxation function used in our work is the autocorrelation of the shear stress tensor, $G(t) = \langle \sigma_{xy}(t)\sigma_{xy}(0) \rangle / (Ak_B T)$ with initial value of this

autocorrelation giving the infinite frequency shear modulus $G_\infty = G(0)$. The angular brackets denote the average over the entire ensemble, with A being the area and $\sigma_{xy}(t)$ the microscopic stress tensor defined as

$$\sigma_{xy}(t) = \sum_{i=1}^N m_i v_i^x(t) v_i^y(t) - \sum_{j>i}^N x_{ij}(t) y_{ij}(t) \frac{\phi'(r_{ij}, t)}{r_{ij}(t)}. \quad (1)$$

The first term on the right-hand side has a purely kinetic origin and is the dominating term at high temperatures, whereas the second term is the excess part and has its origin in particle interactions. Figure 1 shows the normalized stress relaxation function $G(t)$ of a 2D Yukawa liquid at various coupling strengths $\Gamma > \Gamma_c(\kappa)$. It is clear that at short times, $G(t)$ has a zero slope, meaning that liquid response is dominantly elastic. This is followed by a region of fast decay where both the elastic and viscous effects are comparable. At large times, $G(t)$ has become much smaller (within statistical noise) indicating a regime dominated by viscous response and negligible elastic effects. It is also seen from the figure that the relaxation time increases with Γ , implying that elastic response will dominate for longer times as Γ increases. This is mainly due to growing structural order as shown in the inset of Fig. 1. Next, we show our data on the G_∞ calculation in Fig. 2 at various κ . It is interesting to see that unlike shear viscosity, which has a well-defined minimum at $\Gamma_c(\kappa)$ (see Ref. [18]), G_∞ does not have a minimum at any temperature. The contributions coming from both the ideal and excess part of G_∞ are shown in the inset of Fig. 2. At low Γ , the ideal part G_∞^{id} is the dominating term, whereas at high Γ the excess term G_∞^{ex} becomes a major contributor to the overall G_∞ . It is interesting to note that the excess part G_∞^{ex} saturates as Γ increases with the saturation values being higher for the

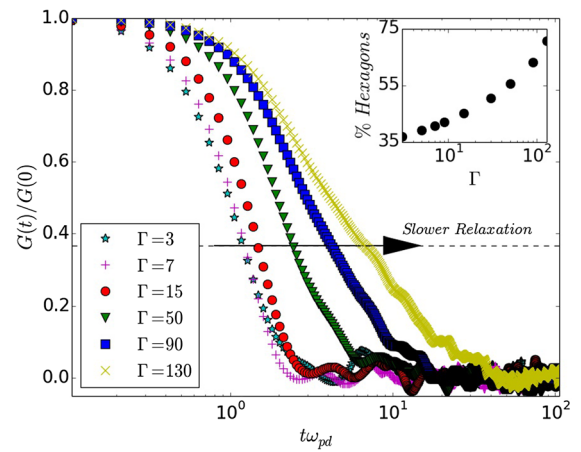


FIG. 1 (color online). Normalized stress relaxation function $G(t)$ for various $\Gamma > \Gamma_c(\kappa)$. The dashed line marks the e -folding time. Inset: Growing hexagonal order in the liquid with Γ .

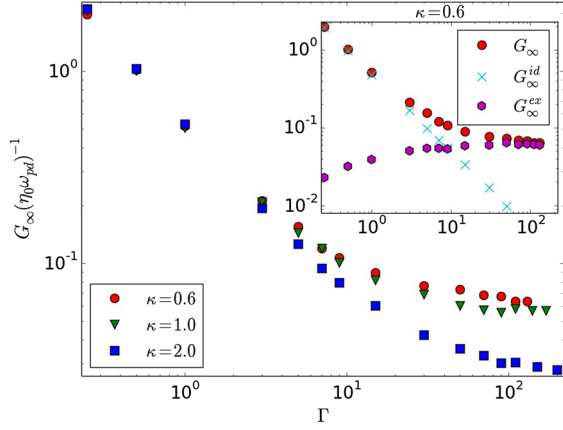


FIG. 2 (color online). Infinite frequency shear modulus G_∞ vs Γ at various κ . Inset: Total, ideal, and excess contributions for the case $\kappa = 0.6$.

cases with lower κ . This implies that a longer range of interaction results in an increase in the infinite frequency elastic response. Hence, Fig. 2 shows that the degree of stiffness in the mechanical response of the liquid is related to the range of interaction potential between the constituent dust grains.

Next, we calculated the shear viscosity η by time integrating the stress relaxation function—a procedure well known as the Green-Kubo formula [26]. Our data for viscosity (not shown here) are qualitatively similar to the data shown in Ref. [18]. The ratio of η to G_∞ then defines an average shear relaxation time or the Maxwell time [27],

$$\tau_M = \frac{\eta}{G_\infty} = \frac{\int_0^\infty G(t) dt}{G_\infty}. \quad (2)$$

Figure 3 shows a plot of τ_M vs coupling strength Γ for three values of κ . Our data show the minimum in τ_M at $\Gamma = \Gamma_c(\kappa)$ similar to the results reported in Ref. [22]. This

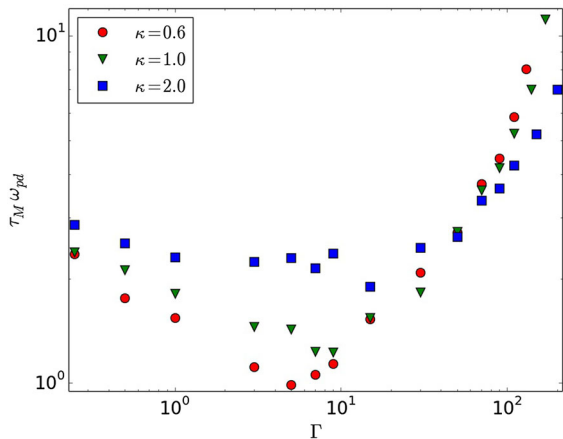


FIG. 3 (color online). Maxwell relaxation time τ_M calculated from Eq. (2), showing a clear minimum around $\Gamma_c(\kappa)$.

means that if one considers τ_M (the relaxation of the total stress autocorrelation) as a measure of elastic response, then it would imply that elasticity will persist for longer times as the weakly coupled limit or $\Gamma \rightarrow 0$ is approached. We, therefore, conclude that τ_M is not a correct measure of elasticity in these liquids as $\Gamma \rightarrow 0$. To identify an appropriate measure of elasticity, we turn our attention to the components of the total stress autocorrelation $G(t)$, namely, the ideal part $G^{\text{id}}(t)$ and the excess part $G^{\text{ex}}(t)$. There is a cross term as well, but its value is negligible at all values of (κ, Γ) . In Fig. 4, we show the relaxation times of the total stress autocorrelation and its two components over the range of Γ from the weakly coupled to the strongly coupled regime. As the liquid nears freezing ($\Gamma \rightarrow \Gamma_m$), $\tau_M^{\text{ex}} \rightarrow \tau_M$ and the shear relaxation is dominantly due to the particle interactions. We find that the relaxation time of the $G^{\text{ex}}(t)$ denoted here by τ_M^{ex} serves as a good measure of elasticity as it goes to zero monotonically as $\Gamma \rightarrow 0$. On the high- Γ side, it rises exponentially with Γ (see inset of Fig. 4) as the liquid approaches the freezing transition. On the other hand, as $\Gamma \rightarrow 0$, the relaxation time of $G^{\text{id}}(t)$ denoted here as τ_M^{id} becomes dominant and is entirely responsible for the origin of τ_M . This means that in the weakly coupled fluid limit, stress relaxation is purely kinetic and has very little contribution coming from particle interactions. To further confirm and strengthen our assertion on τ_M^{ex} being the right indicator for elasticity, we go beyond the observations based on the right asymptotic behavior with Γ and seek a microscopic basis for this behavior by examining the dynamics of the local atomic connectivity.

In solids, phonons are weakly scattered (long-lived), and, hence, they constitute the microscopic origin for vibrations. In liquids, however, they exhibit highly marginalized behavior as they are strongly scattered due to lack of any underlying long-range structural order. As a result,

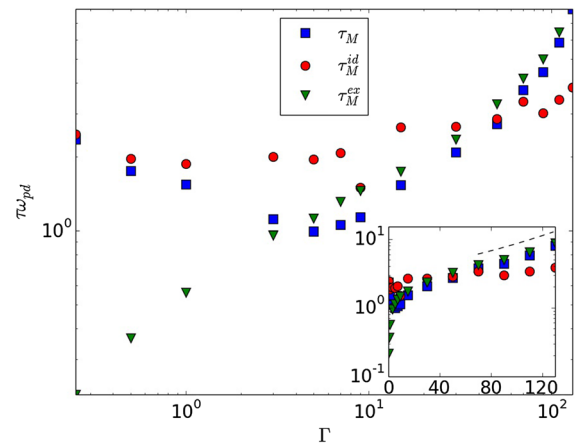


FIG. 4 (color online). Relaxation times of the excess, ideal, and total stress relaxation function for $\kappa = 0.6$. Note that while the excess term τ_M^{ex} continues to rise all the way to the freezing transition where it becomes exponential (see dashed line in the inset), the ideal part saturates to a constant value around $\Gamma_c(\kappa)$.

phonons cannot be used to explain the microscopic origins of viscosity and the infinite frequency shear modulus. One is, thus, led to the following fundamentally important question: What is the microscopic origin for shear relaxation in SCYL? To answer this question, we measure the lifetime of the local atomic connectivity τ_{LC} [23] in SCYL. To calculate τ_{LC} , one first assigns a set of bonds between a central atom and its nearest neighbors at some reference time t_0 . The nearest neighbors here correspond to atoms situated at a distance less than the location of the first minimum in the radial distribution function. Once a reference state is assigned, we track the change in local atomic connectivity, i.e., the central atoms losing some neighbors. As the simulation proceeds, the average coordination number will reduce, and τ_{LC} is extracted as the time duration (elapsed since t_0) in which the average coordination falls by 1. To improve statistics, we have averaged our data over several independent realizations. In this sense, τ_{LC} is the average time during which any atom will lose one neighbor. It was shown in Ref. [23] that above a certain crossover temperature, τ_{LC} converges to the Maxwell time τ_M and is, thus, the microscopic origin of shear relaxation in a range of liquids. However, it should be noted that none of the liquids discussed in that work showed a nonmonotonic behavior in τ_M and, hence, differed in a distinct fashion from our SCYL model. In Fig. 5, we show our data on τ_{LC} calculated at various values (Γ, κ) and make the following interesting observation. At $\Gamma < \Gamma_c(\kappa)$, $\tau_{LC} \rightarrow \tau_M^{ex}$ making τ_{LC} the microscopic origin for the relaxation time of the excess part of stress at these temperatures. Since τ_{LC} corresponds to the time duration where the topology of nearest neighbors remains intact, it is also the duration of the dominant elastic or “solidlike” response. For a comparison, we also show the relaxation time scale of the temporal correlation of the bond-orientation order function Ψ_6 [28]. We note that at the lowest Γ values used in this work, both τ_{Ψ_6} and τ_{LC} tend to converge to τ_M^{ex} with τ_{LC} showing the better overall agreement. At higher values of Γ , both τ_{Ψ_6} and τ_{LC} fail to capture the origin of τ_M^{ex} . These observations directly imply that the relevant shear relaxation time scale, which quantifies the elastic response in these liquids, is τ_M^{ex} , which becomes equal to τ_{LC} at $\Gamma < \Gamma_c(\kappa)$ and approaches the value of τ_M at $\Gamma > \Gamma_c(\kappa)$. It may also be noted that at $\Gamma > \Gamma_c(k)$, τ_{LC} deviates from τ_M^{ex} directly indicating a crossover from a kinetic regime to a potential energy dominated regime. This is a regime where interaction between local networks becomes significant and leads to cancellation of long-range elastic fields [23].

Summary.—We have calculated the infinite frequency shear modulus G_∞ , Maxwell relaxation times (τ_M , τ_M^{id} , and τ_M^{ex}) and the lifetime of the local atomic connectivity τ_{LC} of a 2D SCYL using accurate MD simulations. Our major finding was the microscopic origin of shear relaxation in SCYL, namely, that the lifetime of topology of nearest

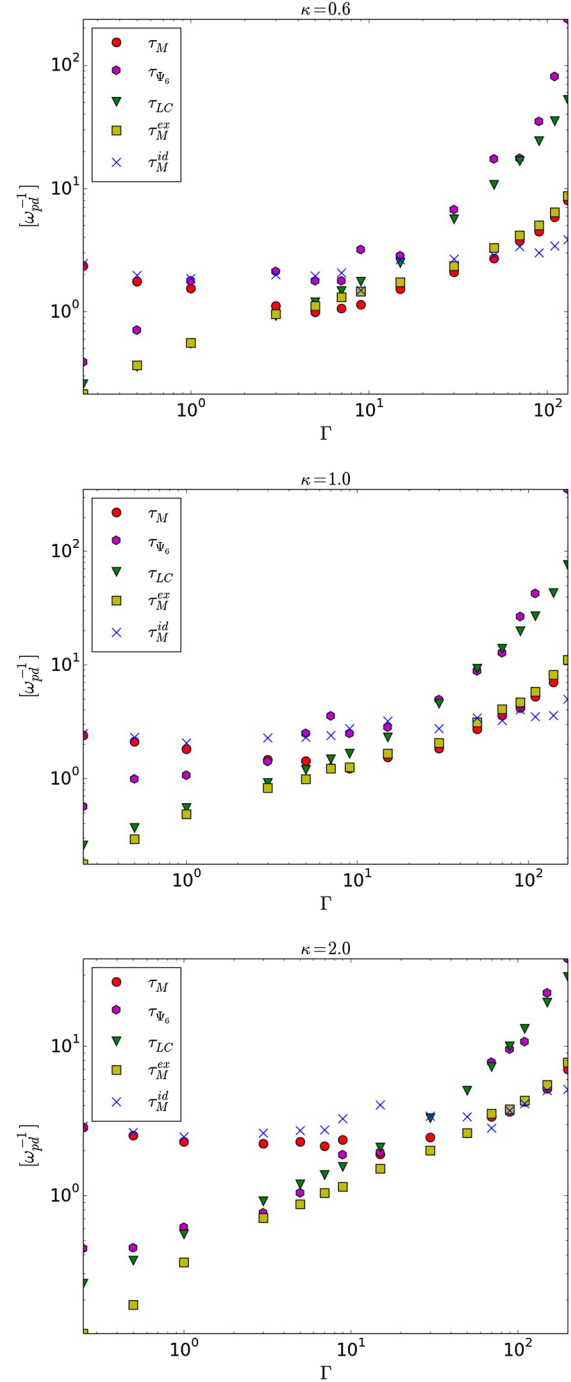


FIG. 5 (color online). Comparison of time scales τ_{LC} , τ_{Ψ_6} , τ_M , τ_M^{ex} , and τ_M^{id} for the cases (bottom) $\kappa = 2.0$, (middle) $\kappa = 1.0$, and (top) $\kappa = 0.6$.

neighbors τ_{LC} is responsible for the relaxation of the excess part of the shear stress. We also provided a solution to the riddle concerning the minimum in τ_M , which renders it unsuitable to quantify the elastic properties of a SCYL approaching the weakly coupled fluid limit $\Gamma \rightarrow 0$. We resolved this issue by proposing that the correct object that quantifies elastic response of such strongly coupled liquids is the relaxation time of the excess part of the shear stress

autocorrelation τ_M^{ex} which goes to zero as $\Gamma \rightarrow 0$ and becomes exponential as the liquid nears the freezing transition. Our assertion is backed by careful measurements of the lifetime of the local atomic connectivity τ_{LC} , which clearly shows that $\tau_M^{\text{ex}} \rightarrow \tau_{\text{LC}}$ below the crossover $\Gamma_c(\kappa)$ directly indicating that τ_M^{ex} is the duration of dominant elastic response. The relaxation of the ideal part of shear stress autocorrelation τ_{id} saturates with $\Gamma > \Gamma_c(\kappa)$, implying a crossover from the kinetic regime to the potential energy regime. We also found that the infinite frequency shear modulus G_∞ does not have a minimum at any temperature as opposed to the viscosity data, which have a well-known minimum around $\Gamma_c(\kappa)$.

We believe our present findings constitute an important step towards improving our understanding of the behavior of strongly coupled Yukawa liquids by providing a new insight and connection between the bulk mechanical response and the underlying microscopic dynamics of such liquids. The results may have wider applicability to other viscoelastic liquids exhibiting a nonmonotonic behavior of Maxwell time with temperature and can form the basis of new research explorations in condensed matter physics and complex plasmas.

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