Annealing glasses by cyclic shear deformation

Pallabi Das, 1 Anshul D. S. Parmar, 1,* and Srikanth Sastry 1

1 Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bengaluru, 560064, India

A major challenge in simulating glassy systems is the ability to generate configurations that may be found in equilibrium at sufficiently low temperatures, in order to probe static and dynamic behavior close to the glass transition. A variety of approaches have recently explored ways of surmounting this obstacle. Here, we explore the possibility of employing mechanical agitation, in the form of cyclic shear deformation, to generate low energy configurations in a model glass former. We perform shear deformation simulations over a range of temperatures, shear rates and strain amplitudes. We find that shear deformation induces faster relaxation towards low energy configurations, or overaging, in simulations at sufficiently low temperatures, consistently with previous results for athermal shear. However, for temperatures at which simulations can be run till a steady state is reached with or without shear deformation, we find that the inclusion of shear deformation does not result in any speed up of the relaxation towards low energy configurations. Although we find that configurations from shear simulations to have properties indistinguishable from an equilibrium ensemble, the cyclic shear procedure does not guarantee that we generate an equilibrium ensemble at a desired temperature. In order to ensure equilibrium sampling, we develop a hybrid Monte Carlo algorithm that employs cyclic shear as a trial generation step, and has acceptance probabilities that depend not only on the change in internal energy but also on heat dissipated (equivalently, work done). We show that such an algorithm indeed generates an equilibrium ensemble.

I. INTRODUCTION

The hallmark of glassy behaviour is the enormous slow down of dynamics upon decreasing temperature as the glass transition is approached. In studies of glass forming liquids through experiments and in computer simulations, such a slow down means that the observed glass transition is always a kinetic phenomenon whereby the liquid falls out of equilibrium in a protocol dependent fashion. Importantly, because glass formers (in particular in computer simulations) fall out of equilibrium too far away from a putative ideal glass transition, definitive validation or refutation of proposed explanations for glassy behaviour becomes difficult [1–5]. A telling example is the growth of length scales that are considered to be associated with the approach to the glass transition. Whereas such length scales are expected to diverge at the glass transition, their growth in the observed range of temperatures is modest, varying by less than an order of magnitude [5]. Thus, extending the range of states that can be analysed is of great importance in developing a better understanding of the behaviour of glass forming systems. The reasons for the difficulty in accessing low temperature states is often expressed in terms of the complex energy landscape possessed by glassy systems [6, 7], and going beyond glass formers, the “rugged energy landscape” problem is of relevance to a wide variety of physical systems and contexts.

Recent years have witnessed encouraging progress in addressing the problem of preparing and simulating glass formers and glasses in well annealed, low temperature (or high density) states. Seminal work by Ediger et al. opened new directions in experiments and simulations in generating deeper energy states in an efficient manner [4–8]. It has been shown experimentally that through physical vapour deposition (PVD) of particles on a substrate, maintained at an optimal temperature (15 % below Tg), glasses that correspond to much lower temperatures compared to conventional methods can be prepared [4–8]. Enthalpic measurements suggest that the PVD technique results in much lower enthalpy and higher density glasses, termed ultrastable glasses, compared to conventional approaches [4–8]. In computer simulations, time scales accessible to conventional molecular dynamics and Monte Carlo simulations are many orders of magnitude shorter than in experiments. Some approaches using non-local moves and other methods have been attempted with varying degrees of success. The experimental PVD method has motivated the corresponding method in *silico* to generate extremely well annealed glass films [16–18], by optimizing deposition rates and substrate temperature. A limitation of this approach, however, is that it is restricted to the specific geometry required, namely that of a film, and the glasses prepared via PVD are inhomogeneous, i.e., the bulk density differs from that of the surface [17]. In simulations of polymeric glasses, the stability is correlated with the high degree of anisotropy, appearing from the layering of polymer along the normal direction to the substrate [19]. More recently, the swap Monte Carlo method [11–13], in which non-local swaps of distinguishable particles are employed to achieve accelerated sampling of configuration space, have been employed with great success in simulating glass forming liquids [20, 22], and also promises to lead to other new simulation approaches [23]. A shortcoming currently of the swap Monte Carlo approach is that it relies on the presence of polydispersity in the simulated systems, although
ways of circumventing this limitation are being explored \[24\]. Even without doing so, the approach allows regimes previously unexplored in simulations to be explored \[25–28\]. These developments have greatly advanced the ability to simulate glass formers at low temperatures, and prompted the exploration of other approaches.

Here, we explore whether the approach to low energy configurations in glass formers can be enhanced by the application of cyclic shear deformation, motivated by results for athermal cyclic shear. The behaviour of glasses (or inherent structures (IS), local energy minima generated by energy minimization of liquid configurations) under (typically, but not restricted to) athermal quasistatic (AQS) shear deformation have recently been investigated in order to study the mechanical behaviour of glasses and related phenomena \[26–38\]. Under cyclic, or oscillatory, shear deformation, the energies of the glasses are found both to decrease from cycle to cycle, or increase, depending on relevant parameters \[29,30\]. A detailed analysis of a model glass by Leishangthem et al. \[30\], with the amplitude of shear deformation as the relevant variable, showed that below the yielding strain amplitude, progressively deeper energy minima are sampled, whereas above the yielding amplitude, energies become larger, accompanied by the formation of shear bands \[31\]. The lowest energy, homogeneous, structures are attained at (but below) the yielding point. This observation (consistent with various theoretical investigations describing the yielding point as a limit of vanishing or low barriers to rearrangements \[32,33\]) suggests cyclic deformation at suitably chosen shear amplitudes as an approach to generate low energy configurations. In the present work, we investigate this possibility. In order to incorporate thermal relaxation and to explore the role of additional parameters, we study oscillatory shear deformation of liquids at finite temperature and shear rates.

II. MODEL AND METHODS

We perform non-equilibrium molecular dynamics simulations (NEMD) to shear deform a model glass former at finite temperatures and strain rates. The trajectories are generated via the SLLOD algorithm \[45\], employing LAMMPS \[46\] with a Nosé-Hoover thermostat, or (for simulations of equilibrium sampling) by an implementation of the Gaussian iso-kinetic thermostat as described in \[47\]. We study the Kob-Andersen 80:20 mixture \[48\] with a quadratic cutoff at \(\tau_{\alpha\beta} = 2.5\sigma_{\alpha\beta}\), applying Lees-Edwards periodic boundary conditions \[49\]. The model parameters are \(\epsilon_{AB}/\epsilon_{AA} = \epsilon_{BA}/\epsilon_{AA} = 1.5\), \(\epsilon_{BB}/\epsilon_{AA} = 0.5\), and \(\sigma_{AB}/\sigma_{AA} = \sigma_{BA}/\sigma_{AA} = 0.8\), \(\sigma_{BB}/\sigma_{AA} = 0.88\). Energy values reported are energies per particle, in units of \(\epsilon_{AA}\). Further details may be found in \[49\].

The initial liquid configurations are generated via equilibrium molecular dynamics (MD) simulation (typically, at temperature \(T = 0.466\)). Then, these configurations are subjected to oscillatory shear deformations for a range of temperatures, strain rates and amplitudes, solving the SLLOD equations:

\[
\dot{r}_i = \frac{p_i}{m} + r_i \nabla v \\
\dot{p}_i = \frac{F_i}{m} - p_i \nabla v - \alpha(t) p_i
\]

where the strain rate tensor has only the \(xy\) component being non-zero, and given by \(\gamma_{xy}(t) = \gamma_{\max} \sin(\omega t)\), where \(\omega\) is the frequency, and \(\gamma_{\max}\) is the amplitude of strain. The strain rates \(\dot{\gamma}\) reported are the strain rate values at the initial time of each cycle, i.e. \(\dot{\gamma} = \gamma_{\max} \omega\). The friction coefficient \(\alpha\) depends on the thermostat used. The relaxation time from the equilibrium MD simulation is denoted as \(\tau\), whereas the time in the NEMD simulation is denoted by \(t\). We consider \(N = 4000\) particles at the reduced density \(\rho = 1.2\) and perform simulations for a range of temperatures \((T \in [0.1, 0.4])\) across the Kauzmann temperature estimated in previous work to be \(T_K \approx 0.3\), shear rates \((\dot{\gamma} \in [10^{-6}, 10^{-3}]\)), and strain amplitudes \((\gamma_{\max})\) up to 0.06. We perform conjugate gradient minimization on the simulated (stroboscopic) configurations to obtain energy minimum configurations (inherent structures). We evaluate the potential energy of sheared liquid configurations and inherent structures, stress anisotropy and two dimensional pair correlation functions to characterize their anisotropy, if present. The error bars on \(\gamma_{\max}\) indicate the grid spacing with which we sample \(\gamma_{\max}\). The error bars on energies are the standard error of the mean of block averaged energies, with 20 block considered within the measurement window (see Appendix for additional details).

In addition to the cyclic shear simulations, we also perform constant temperature MD simulations using the Gaussian isokinetic thermostat and employing LAMMPS \[46\] with a Nosé-Hoover thermostat.

III. RESULTS

We carry out a series of simulations for different shear amplitudes, for each of a set of shear rates and temperatures. The grid of values is limited by the significant computational effort for each data set. In order to monitor the extent of structural relaxation, we compute the average IS energies as a function of cycles, and map the IS energies to corresponding temperatures, as explained below.

A. Cyclic shear simulations

To find out the amplitude dependence of the IS energy (which we report stroboscopically, i.e., at the end of each cycle, unless otherwise noted), we show in Fig. \[1\]...
the IS energies ($e_{IS}$), for temperature $T = 0.3$ and strain rate $\gamma = 10^{-5}$. Fig. 1 (a) shows that with the increase in strain amplitude the system descends towards lower energy minima, up to a particular amplitude, whereas for larger amplitudes the energies begin to increase. Fig. 1 (b) shows the values of the IS energies at a large time of $t \sim 10^7$, as a function of strain amplitude $\gamma_{\text{max}}$, with $\gamma_{\text{max}} = 0.035$ generating the lowest energy configurations. As shown in the Appendix, Fig. A1, $\gamma_{\text{max}} = 0.035$ displays characteristics of the yield strain amplitude observed earlier in AQS simulations[60] and we henceforth refer to the $\gamma_{\text{max}}$ value displaying the lowest energies as the yield amplitude. Corresponding data for other cases are presented in the Appendix. We note that the decrease of energies is generally logarithmic, a feature observed in aging systems, granular compaction, etc. [50, 53].

The long time values of IS energies vs. strain amplitude, obtained as an average over the interval from $t = 8 \times 10^6$ to $t = 10^7$. The strain amplitude for which the energy is lowest is identified as the optimal amplitude for annealing. (c) The strain amplitude for minimum IS energy is a decreasing function of temperature. (d) The minimum inherent structure energy attained vs. temperature, shown for three different shear rates. The results indicate that the optimum temperature for annealing is $T \approx 0.35$.

We next consider the strain rate and temperature dependence of the optimal strain amplitude considering a range of strain rates ($\dot{\gamma} \in [10^{-3}, 10^{-6}]$) and temperatures ($T \in [0.25, 0.4]$). Although with limited data, shown in the Appendix, we see that with increasing strain rates, the yield strain shifts towards higher values (see Appendix, Fig. A2-A5), consistently with previous results [54, 55]. Likewise, as the temperature is lowered the yield strain amplitude shifts towards higher strain amplitudes, as shown in Fig. 1 (c). For each strain rate, we consider the IS energies obtained at the optimal strain amplitude $\gamma_{\text{max}}$ and plot it as a function of temperature in Fig. 1 (d) (see appendix, Fig. A2-A5). Similar to observations for PVD [67], we find the maximum extent of annealing for $T = 0.35$, near the estimated Kauzmann temperature ($T_K \approx 0.3$).

Though the optimal strain amplitude depends on the temperature and rate, we focus below on the amplitude $\gamma_{\text{max}} = 0.035$, the optimal value for strain rate $10^{-5}$ at $T = 0.3$. The evolution of the IS energy for different shear rates (Fig. 2 (a)) shows that for higher shear rates the energies in the initial times are lower, but the rate of decrease is marginally larger for lower shear rates. In order to estimate the efficiency of the approach, we need a mapping of the inherent structure energies and temperatures. For this, we use the observation [60] that the inherent structure energies at low temperatures display the behaviour

$$e_{IS}(T) = E_\infty - A/T,$$

where $E_\infty$ is the extrapolated infinite temperature IS energy and $A$ represent the slope of $e_{IS}$ vs. $1/T$ (see Appendix). We estimate the equilibrium temperature corresponding to a given inherent structure energy using this relationship. As an extrapolation, however, the meaning of the temperature so estimated should be treated with due caution (see Appendix for further details). Next, we compute relaxation times corresponding to a given temperature using the Vogel Fulcher Tamman relation (VFT) expression $\tau = \tau_0 \exp \left[\left(\frac{K_{VFT}}{T/T_{VFT}} - 1\right)^{-1}\right]$ where parameters $\tau_0$, $K_{VFT}$ and $T_{VFT}$ are obtained from fits to MD simulations [57] (see Appendix). A comparison of the estimated temperature reached for a given simulation time with the relaxation time at that temperature provides a way of judging the extent to which cyclic shear may accelerate the accessing of low energy configurations. Fig. 2 (b) shows the estimated temperatures vs. simulation time, along with reference curves that indicates the dependence of the relaxation times on temperature. A long run of duration $t \sim 6 \times 10^8$ at $\dot{\gamma} = 10^{-5}$ shows the lowest temperature accessed is approximately $T = 0.34$ ($e_{IS} \approx -7.08$, to be compared with the lowest estimated value of $-7.15$; see Appendix). We show extrapolated VFT curves for two cases in Fig. 2 (b). The first curve (magenta) is the VFT fit to relaxation times for temperatures above $T_{MCT} = 0.435$, which is extrapolated for lower temperatures. A comparison with this VFT fit leads to the conclusion that the relaxation to low energy configurations is significantly accelerated by the application of cyclic shear. To make a direct comparison, MD runs are performed at low temperatures (reported in [57]), with the lowest temperature being $T = 0.365$. These simulations reveal that the temperature dependence of relaxation times undergoes a crossover, with low temperature relaxation times being significantly smaller than the VFT extrapolation from temperatures above $T = 0.435$. The relaxation times over this extended temperature range are also fitted to the VFT form, which
is also shown in Fig. 2 (b) (maroon curve). A comparison of the cyclic shear results with results from low temperature MD simulations indicates that, contrary to the earlier conclusion, no significant acceleration is obtained through the application of cyclic shear.

Although the application of cyclic shear deformation does not therefore appear promising as an approach to performing accelerated sampling at low temperatures, it does lead to overaging when simulations are performed at temperatures lower than $T = 0.3$ considered above. We thus consider a series of temperatures $T = 0.1, 0.15, 0.2, 0.25, 0.3, 0.4$, and perform cyclic shear at each temperature for a range of strain amplitudes $\gamma_{\text{max}}$ and shear rate $\dot{\gamma} = 10^{-5}$. For each temperature, we consider the IS energies reached for a simulation time $t \approx 10^7$, and compare with the corresponding results for MD simulations. Results shown in the Appendix (Fig.s A4 - A6) reveal that the gap between the energies reached in MD simulations and cyclic shear simulations increases upon lowering the temperature. To quantify this, we compute the difference between the energy reached at $t \approx 10^7$ and the initial value, $\Delta e_{\text{IS}}$, in MD and cyclic shear simulations respectively. The ratio $\Delta e_{\text{IS}}^{\text{md}}/\Delta e_{\text{IS}}^{\text{cs}}$, shown in Fig. 2 (c), indeed grows as the temperature decreases, indicating a greater degree of overaging induced by the cyclic shear deformation, the lower the temperature.

**B. Properties of sheared configurations**

Apart from the question of whether cyclic shear induces acceleration of relaxation, addressed in Sec. 3.1 above, it is of importance to ascertain whether the properties of the sheared liquids are comparable to the equilibrium liquid. We perform a comparison of properties of the sheared liquid and that simulated with conventional MD. Results presented here and in the Appendix show that the configurations generated by cyclic shear are isotropic, homogeneous, and have properties that are indistinguishable from the equilibrated liquid configurations. We have chosen $T = 0.4$ (and higher temperatures) for a comparison of the structures generated by conventional constant temperature MD and cyclic shear, at which the liquid can easily be equilibrated with moderate effort in a constant temperature molecular dynamics simulation and (as described later) cyclic shear simulations reach steady states within the simulated time window. For cyclic shear, we have kept our shear rate fixed at $\dot{\gamma} = 10^{-5}$ and based on short runs across different strain amplitudes, identify $\gamma_{\text{max}} = 0.005$ as being a reasonable choice based on data shown in Fig. A2 for comparison with MD simulations.

![Figure 2](image-url)  
**FIG. 2.** Inherent structure energies $e_{\text{IS}}$ vs. time for different shear rates and different damping parameters $(Q)$, at the simulation temperature $T = 0.3$. (b) The energies $e_{\text{IS}}$ is transformed to temperatures corresponding to those energies for equilibrated samples. Also shown are VFT fits to relaxation times obtained in MD simulations, (i) above $T = 0.435$ (magenta line), and (ii) for temperatures extending to $T = 0.365$ (maroon line). (c) The ratio of the difference between the energy reached at ($t \sim 10^7$) and the initial value, for MD and cyclic shear ($\Delta e_{\text{IS}}^{\text{md}}$ and $\Delta e_{\text{IS}}^{\text{cs}}$ respectively), as a function of the simulation temperature.

![Figure 3](image-url)  
**FIG. 3.** The $e_{\text{IS}}$ energies obtained from the equilibrium MD is compared to the $e_{\text{IS}}$ energy obtained from sheared configurations at amplitudes of $\gamma_{\text{max}} = 0.003, 0.005$. The energies show good quantitative agreement. The temperature varies in the range $[0.4 - 0.45]$, where the system can be equilibrated easily by normal molecular dynamics. The shear rate has been kept fixed at $\dot{\gamma} = 10^{-5}$. The inset shows the inherent structure energies against inverse temperature, indicating that the energy obeys a $1/T$ dependence on $T$. 
In Fig. 3, we compare the average inherent structure energy obtained from molecular dynamics simulations and finite temperature, finite shear rate, cyclic deformation, as a function of temperature, and show that the energies in these cases are comparable to each other and follow $1/T$ behaviour in the low temperature range.

Fig. 4 shows that the partial radial distribution functions of the inherent structures obtained by NVT MD and cyclic shear simulations agree with each other quantitatively, which implies that the structures generated by cyclic shear are the same as those generated by MD.

We also show, in Fig. 5, that the vibrational density of states of configurations obtained by NVT MD and cyclic shear at $T = 0.4$ are the same, whereas they are clearly different from those at $T = 0.6, 1.0$ obtained from MD simulations. (b) The difference of the DOS at different temperatures from the cyclically sheared configurations at $T = 0.4$, indicating that MD and cyclic shear results at $T = 0.4$ are indistinguishable.

Fig. 6. (a) For strain amplitudes lower than or close to the yielding amplitude, stress anisotropies for strain rate $10^{-5}$ compare with those of isotropic inherent structures (indicated by the horizontal line). (b) Variation of density in the shear direction indicating that the system is homogeneous in all cases.

We next examine possible anisotropies in the structures we generate. The ultrastable glasses produced by physical vapor deposition (PVD) method have shown features that can be connected to more anisotropic packing, compared to its ordinary glass counterpart formed by cooling the liquid. Since we perform shear in a given plane, anisotropies are also possible in our case. To characterise anisotropy and inhomogeneity, we first consider the stress anisotropy, which is defined as $SA = (S_1 - S_2)/(S_1 + S_2 + S_3)$, where $S_i$ ($S_1 > S_2 > S_3$) are the eigenvalues of the stress tensor. Excepting for very large strain amplitudes, we find the stress anisotropies to be small, and comparable to those of inherent structures quenched directly from liquid configurations, as shown in Fig. 6 (a). We also test for the possibility of shear localisation accompanied by inhomogeneities in the local density. Density values obtained for slabs in the shear direction show no evidence of density inhomogeneities (as they do beyond the yield strain in AQS simulations [40], although for larger samples), as shown in Fig. 6 (b).

Additional comparisons presented in the Appendix (A.5 and A.6) show that the IS configurations obtained by cyclic shear are isotropic, and that they exhibit the same response to shear (in the form of the distribution of strain required to undergo a plastic rearrangement) as those obtained from conventional MD. Finally, in Appendix A.7 we show results from applying shear in alternating shear planes ($xy, xz, and yz$) which does not lead to significant change in relaxation of the energy, or the stress anisotropy.

C. Equilibrium sampling

The results described above illustrate that configurations generated by cyclic shear, under the right condi-
tions, display properties that are indistinguishable from those obtained from MD simulations, an observation that is extremely useful (see also [52]). Nevertheless, it does not guarantee that an equilibrium ensemble is always generated, which is desirable. In order to achieve this, we develop an equilibrium Monte Carlo sampling scheme which guarantees equilibrium sampling, and demonstrate that it can be implemented as an efficient method and generates equilibrium ensembles of configurations.

In order to compare with equilibrium properties, we consider $T = 0.4$, at which it is relatively easy to equilibrate using a conventional MD (NVT) simulation. Based on results shown in the Appendix, we choose a strain amplitude, $\gamma_{\text{max}} = 0.005$ and perform cyclic shear at $\gamma_{xy} = 10^{-3}$ and compare with molecular dynamics simulations, both using the Gaussian iso-kinetic thermostat. Fig. 7 (a) shows the evolution of the IS energy for sheared simulations as well as for molecular dynamics, averaging results over 5 independent simulations. We note that sheared simulations reach steady state values that correspond to the expected equilibrium value. As shown in Sec. III B, this is true for a range of temperatures, and further, structural and vibrational properties of sheared and MD configurations are indistinguishable. In one of the shear simulations, the energies drop to significantly lower values at longer times, as also shown in Fig. 7 (a). This results from crystallisation [59], as we confirm from analysis presented in the Appendix (A.9). We thus check all simulation results to ensure that the analysed trajectories are free of a significant degree of crystallisation. Fig. 7 (b) shows that the distribution of energies in the steady state for the cyclic shear simulations is identical to the MD trajectory.

Next we describe an equilibrium sampling algorithm employing cyclic shear, which is in the spirit of hybrid Monte Carlo (HMC) [64]. In hybrid Monte Carlo, a molecular dynamics trajectory is employed as a ‘generation step’ for a trial move. At the end of each such generation step, a Metropolis Monte Carlo acceptance of the resulting final state is attempted. As with most Monte Carlo algorithms, one must obey detailed balance. In the original hybrid Monte Carlo algorithm, detailed balance is guaranteed by the use of Hamiltonian dynamics, which is time reversible, and phase space volume preserving. However, nonequilibrium simulations, such as ours do not obey these properties. Although SLLOD equations preserve phase space volume and are reversible, thermostatting leads to a compression of phase space volume [61] (see Appendix for details). We modify the HMC acceptance probability by compensating for the phase space volume contraction. Representing a point in phase space by $\Gamma$, and with the phase space compression factor $\Lambda(\Gamma) = \frac{\partial \Gamma}{\partial \Gamma}$, the change in phase space volume is given by

$$C(t) = \exp \left( \int^t \Lambda(s)ds \right) = e^{\frac{\Delta Q}{k_B}}$$

(3)

where $\Delta Q$ is the change in heat (heat dissipation $Q_d = -\Delta Q$). Thus, the acceptance probability for a trial phase space point $\Gamma' = (x', p')$ starting with $\Gamma = (x, p)$, that ensures detailed balance, is

$$p_A(\Gamma \to \Gamma') = \min \{1, \exp(-\gamma \Delta U)\exp(\beta_s \Delta Q)\}$$

$$= \min \{1, \exp(-\beta_s \Delta W)\}$$

$$= \min \{1, \exp(-\beta_s \Delta \Phi)\exp(-\beta_s \Delta K)\exp(\beta_t \Delta Q)\}$$

where $U$ is the internal energy, $\Phi$ the potential energy, $K$ the kinetic energy, $\Delta W$ the work done, $T_s = 1/k_B \beta_s$ the sampling temperature. The final, general, expression holds even when the thermostat temperature $T_t = 1/k_B \beta_t$ is not the same as the sampling temperature $\beta_s$, a possibility permitted and exploited in HMC schemes. The same acceptance rule can be arrived at, for systems that obey microscopic reversibility, using Crooks theorem [62], as discussed in [63]. The resulting algorithm in the present case involves the following steps each cycle: (1) Generate velocities from a Maxwell distribution corresponding to the temperature at which we perform the SLLOD cyclic deformation ($\beta_t = \beta_s$ in this work), for each cycle regardless of the acceptance of the previous trial configuration. (2) Perform a cycle of shear deformation with the thermostatted SLLOD equations of motion. (3) Compute the change in total energy, heat or equivalently, the work done during the cycle. (4) Accept or reject the final configuration according to the acceptance probability in Eq. 4. Note that the heat can be computed by integrating $\Lambda$ as in Eq. 4 which in turn is given in terms of the friction coefficient $\alpha$ used in thermostatting the dynamics, as $\Lambda = -3N\alpha$ where $N$ is the number of particles. The work done can be computed by integrating the stress $\sigma$ over the cycle: $\Delta W = \int V \sigma_{xy}(s)(s)\hat{\gamma}_{xy}(s)ds$ where $V$ is the volume, $\hat{\gamma}_{xy}$ is the shear rate.

We next describe results that demonstrate that the algorithm described generates an equilibrium ensemble effectively. We first consider the case $T = 0.4$, with $\gamma_{\text{max}} = 0.005$, $\hat{\gamma}_{xy} = 10^{-3}$, considered earlier. Fig. 7 shows IS energies, averaged over five independent runs, with Monte Carlo sampling, in addition to the MD and shear results described above. We find that indeed, the equilibrium sampling results agree with the molecular dynamics and cyclic shear simulations without equilibrium sampling. We next consider shear simulations without and with equilibrium sampling at $T = 0.37$, at which molecular dynamics simulations are harder, since the relaxation time is $\tau = 2.3 \times 10^6$. Results shown in Fig. 7 (c), indicate that indeed, the shear simulations reach steady state values of the IS energy close to $-7.05$, which is the expected value based on Eq. 2 and obtained from MD simulations reported in [57]. Although for results presented thus far, cyclic shear without Monte Carlo sampling also generates results indistinguishable from cyclic shear with Monte Carlo sampling, this need not
be the case. In the Appendix, we show that energies obtained under large amplitude shear deviate from the expected equilibrium values, whereas with Monte Carlo sampling, values close to expected equilibrium values are generated.

We note from Eq. 4 that the acceptance probability depends on the (extensive) work done during a cycle and not the change in energy. This poses a potential problem for large systems. Indeed, as shown in the Appendix, we find that for the case considered so far, $N = 4000$, the acceptance rate is negligible with $T = 0.3$, $\gamma_{\text{max}} = 0.03$, $\dot{\gamma}_{xy} = 10^{-3}$. For $N = 500$, the work done fluctuates around zero (with a small positive mean), and the acceptance rate is sufficiently large.

We discuss two strategies that lead to feasible acceptance rates for larger systems and demonstrate them for $N = 4000$. The first strategy is to perform shear for a randomly chosen subvolume of a size that leads to feasible acceptance rates. The second strategy is to adaptively modify the strain amplitude to achieve a desired acceptance rate. In implementing the first strategy, for each cycle, we randomly pick the centre of a cubic subvolume of pre-specified size. During the shear cycle, the rest of the system is frozen and strained affinely, whereas the subvolume is subjected to SLLOD dynamics at the chosen temperature and shear rate. At the end of the cycle, the entire system is simulated with normal unsheared molecular dynamics for a specified duration. We choose the subvolume to be of linear dimension equal to half the box size $L$ (1/8 of the total system) and the duration of molecular dynamics in the second step to be 1/10 of the cycle period. As before, we perform cyclic shear simulations for $T = 0.4$ and $T = 0.37$, with $\gamma_{\text{max}} = 0.005$ and $\dot{\gamma}_{xy} = 10^{-3}$. A single trajectory is simulated in each case. Fig. 8 (a) shows that indeed this method works efficiently to equilibrate the system in both cases to the correct value of the inherent structure energy. Though the following observations need to be verified by better averaging, we note that cyclic shear without sampling results in higher energies for $T = 0.37$. With sampling, the asymptotic range of energies is reached by $t \sim 2.5 \times 10^6$, indicating a factor of 10 speed up. As earlier results demonstrate, however, the speed-up increases dramatically with a lowering of the target temperature. The goal here, however, has been to present evidence of effective equilibrium sampling.

In implementing the strategy of adaptive strain amplitude, we choose a cutoff for the acceptance ratio, which is evaluated over $10 - 20$ cycles. If the acceptance ratio is below the cutoff, the strain amplitude $\gamma_{\text{max}}$ is reduced, whereas if it is above, it is increased. We test this approach for $T = 0.3$, choosing three different cutoff values of 0.3, 0.5 and 0.85. The $\gamma_{\text{max}}$ fluctuate around values 0.015, 0.01 and 0.001 in these cases. As shown in Fig. 8 (b), in each case, one obtains a logarithmic relaxation of the energy as in the earlier case of $\gamma_{\text{max}} = 0.035$ but less efficiently by roughly a factor of 10. An adaptive strategy that targets the degree of annealing, rather than acceptance rate, may thus be more desirable, and needs to be explored.

D. Discussion and Conclusions

To summarise, we have explored the possibility of generating low energy configurations by the application of cyclic shear deformation, more efficiently than conventional MD simulations. In the range of temperatures ($T \geq 0.365$) where equilibrium MD simulations can be
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FIG. 8. Equilibrium sampling for a system of \( N = 4000 \) particles by performing cyclic shear (a) for a randomly chosen subvolume and (b) employing adaptive modification of shear amplitude.

performed for the model glass former studied \[57\], our results indicate that cyclic shear does not lead to an accelerated approach to low energy configurations. Nevertheless, our results show that cyclic deformation at low temperatures (below the estimated ideal glass transition) leads to accelerated relaxation to low energy structures, the degree of which increases with decreasing temperature. These results may help rationalise conflicting results regarding overaging of glasses \[64, 65\] and are of relevance for understanding mechanically induced aging of glasses in general. Our results demonstrate that, at the temperatures investigated, cyclic shear simulations generate configurations that are indistinguishable from those generated by conventional MD simulations. We have further developed an equilibrium sampling method based on cyclic shear as a trial generating step, and demonstrated that it works effectively to generate equilibrium ensembles of configurations. We have presented strategies that make it generally feasible to employ the algorithm, and demonstrated their effectiveness. This algorithm also suggests a general methodology for employing driving of various kinds for accelerating dynamics, with generalised cyclic deformation, including bulk strain, being an obvious example. Under what conditions such driving may result in accelerated sampling remains an open question to be understood.

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**APPENDIX**

1. **Characterization of the optimal strain amplitude**

   Onset of yielding in athermally sheared glasses has been studied by considering the energy and stress within a strain cycle and as function of cycles. At the yield strain amplitude \( (\gamma_y) \), the system accesses the minimum energy states based on past work\[30\]. Beyond the yielding point, the location of the minimum of energy shifts from zero strain to finite strain values, and the area enclosed by the stress-strain curve becomes finite, indicating the onset of plasticity in the system. We show here that the optimal strain amplitude which we identify as the strain at which the inherent structure energy is minimum (stroboscopically) also displays the characteristic features mentioned above. Note that in the steady state, the evolution of the inherent structure energy within a cycle is expected to be symmetric with respect to strain. In Fig. [A1] we show the variation of energy at some intermediate time at which a steady state has not necessarily been reached. The average \( e_{IS} \) we report as at time \( t \approx 10^7 \) corresponds to the average energy calculated within a time window of \( t \approx 8 \times 10^6 - t \approx 10^7 \). The Error bars shown are the standard error of the mean of block averaged energies obtained for 20 blocks within this time window. At the highest temperature, \( (T=0.4) \) as the system equilibrates faster, we have chosen the time window to be \( t \approx 2 \times 10^5 - t \approx 6 \times 10^5 \) and indicate the average within this block to be the long time average.

2. **Dependence on shear amplitude and rate**

   In this section, we show results of the inherent structure energy variation with time for a range of temperatures and strain rates. The deformation amplitude corresponding to the minimum \( e_{IS} \) in a long time window is identified as the optimal amplitude. As noted earlier, such an optimal strain amplitude shares characteristics with the yielding strain amplitude previously studied in athermally sheared glasses. The optimal point shifts to higher values of strain amplitude as the strain rate is decreased and it shifts to a lower value as the temperature is increased. At the highest temperature, even though we have analysed amplitudes below \( \gamma_{max} = 0.005 \), the behavior for such amplitudes are not significantly distinguishable from that of \( \gamma_{max} = 0.005 \) and no clear minimum in the evaluated energies is present. However, above \( \gamma_{max} = 0.005 \), the energies increase to higher than the equilibrium energy at \( T=0.4 \), and hence we identify for this temperature \( \gamma_{max} = 0.005 \) as the optimal amplitude.
FIG. A1. (a) Inherent structure energy variation within a cycle for different amplitudes at a fixed rate and a fixed temperature. The energy minimum at zero strain shifts to finite strain values above a certain strain amplitude. (b) Variation of stress $\sigma_{xy}$ of inherent structures over a cycle. After a certain amplitude of strain, the stress-strain curves begin to enclose a finite area. (c) The optimal strain identified in the manuscript is the location of the minimum in the energy at zero strain is consistent with criteria for the yield strain in earlier work.

FIG. A2. (a)-(c) The evolution of IS energy for different shear rates has been shown for $T = 0.4$. The amplitude at which the long time energy value reaches a minimum is identified as the optimal amplitude $\gamma_y$. (d) The long time values of IS energies vs. strain amplitude, obtained as an average within a time window from $t = 2 \times 10^5$ to $6 \times 10^5$. The evolution of IS energy for molecular dynamics at $T = 0.4$ is shown in (c) for comparison (red line).
FIG. A3. (a)-(d) The evolution of IS energy for different shear rates has been shown for $T = 0.35$. The amplitude at which the long time energy value reaches a minimum is identified as the optimal amplitude $\gamma$. (e) The long time values of IS energies vs. strain amplitude, obtained as an average for $t = 8 \times 10^6$ to $t = 10^7$. The evolution of IS energy for molecular dynamics at $T = 0.4$ is shown in (c) for comparison (red line).

FIG. A4. (a)-(d) The evolution of IS energy for different shear rates has been shown for $T = 0.3$. The amplitude at which the long time energy value reaches a minimum is identified as the optimal amplitude $\gamma$. (e) The long time values of IS energies vs. strain amplitude, obtained as an average for $t = 8 \times 10^6$ to $t = 10^7$. The evolution of IS energy for molecular dynamics at $T = 0.4$ is shown in (c) for comparison (red line).
FIG. A5. (a)-(d) The evolution of IS energy for different shear rates has been shown for $T = 0.25$. The amplitude at which the long time energy value reaches a minimum is identified as the optimal amplitude $\gamma_y$. (e) The long time values of IS energies vs. strain amplitude, obtained as an average for $t = 8 \times 10^6$ to $t = 10^7$. The evolution of IS energy for molecular dynamics at $T = 0.4$ is shown in (c) for comparison (red line).

FIG. A6. (a)-(c) The evolution of IS energy for the three lowest temperatures ($T = 0.1, 0.15, 0.2$) is shown. The amplitude at which the long time energy value reaches a minimum is identified as the optimal amplitude $\gamma_y$. The evolution of IS energy for molecular dynamics at $T = 0.4$ is shown for comparison (red lines).
3. Equilibrium Molecular Dynamics: Relaxation time and configurational entropy

A comparison of the time scales accessed by the non-equilibrium MD (NVT-SLLOD, NEMD) simulations with the equilibrium NVT-MD simulation results is an important aspect of our analysis. In Fig. A7 (a), we show VFT fits to the relaxation times, first by considering temperatures only for $T > T_{MCT}$ ($\tau_0 = 0.3101$, $K_{VFT} = 0.2243$, $T_{VFT} = 0.2989$). The VFT fits to the high temperature data clearly overestimate the relaxation times for $T < T_{MCT}$. On the other hand, for the VFT fit to the full range ($\tau_0 = 0.1175$, $K_{VFT} = 0.1383$, $T_{VFT} = 0.2592$), the VFT form does not provide a good description of the data at lower temperatures. The fit values are used in our analysis in the manuscript. Fig. A7 (b) shows data (from [56]) for the configurational entropy density vs. inherent structure energy and a quadratic fit (logarithm of a Gaussian density of states). From the shown data and the fit, the configurational entropy vanishes at the Kauzmann energy of $e_{IS} = -7.15$.

![Figure A7](image1)

**FIG. A7.** (a) Relaxation times from molecular dynamics simulations vs. temperature, and the corresponding fit to the VFT form. (b) The configurational entropy density as a function of the inherent structure energy, and a quadratic fit. The extrapolated value of IS energy at which configurational entropy vanishes is ($\approx -7.15$).

4. Correspondence between inherent structure energies and temperatures

In order to obtain an estimate of the temperature to which the inherent structures we generate correspond, we use the observation [56] that inherent structure energies at low temperatures vary as $1/T$. Fitting the energies to the form $e_{IS}(T) = E_\infty - A/T$, we are able to map IS energies and temperatures, as illustrated in Fig. A8. The fit parameters are $E_\infty = -6.7264$ and $A = 0.12065$.

![Figure A8](image2)

**FIG. A8.** (a) Temperature dependence of the inherent structure (IS) energy for a liquid equilibrated in a molecular dynamics simulation. The equilibrium molecular dynamics simulation data has been fitted below temperature $T = 0.7$ to obtain a mapping between the IS energy and temperature, which is used to map the IS energy vs. time data in panel (b) to the temperature values in panel (c). Panel (c) also shows the VFT relationship between temperature $T$ and relaxation times $\tau$. 
5. Structural analysis

We compute the radially averaged and two dimensional (partial) pair correlation functions, for stroboscopic configurations, in order to analyse the structure. For temperature $T = 0.3 \gamma_{xy} = 10^{-5}$, $\gamma_{\text{max}} = 0.035$ has been identified as the yielding strain amplitude. For this amplitude, the radially averaged pair correlation function is calculated after 0 (newly quenched from the liquid), 5, 50 and 500 cycles. The increase in the number of shear cycles corresponds to a decrease in energy and the temperature. The pair correlation functions show very small amounts of change, comparable to what is observed in the equilibrium liquid at different temperatures (Fig. A9).

We also calculate the two dimensional radial distribution function ($g(x,y)$), in the $xy$- (shear) plane, defined as

$$g(x,y) = \frac{1}{2N\rho} \times \left\langle \sum_{i=1}^{N-1} \sum_{j \neq i}^{N} \delta(x - (x_i - x_j)) \delta(y - (y_i - y_j)) \theta(a - |z_i - z_j|) \right\rangle, \quad (1)$$

where "\langle \rangle" represents the averaging over independent samples. $x_i$, $y_i$, and $z_i$ are coordinates of particles. A pair of particles is considered to be in the same plane if the separation between them does not exceed a threshold value $\alpha = 0.2\sigma_{AA}$, which is enforced by the Heaviside function above.

As shown in Fig. A10, these correlation functions do not reveal any indications of anisotropy.

FIG. A9. The partial pair correlation functions of the liquid configurations at the end of different cycles compared with the initial configuration.
FIG. A10. Two dimensional, partial pair correlation functions in the shear plane for (left panel) the initial configurations at $T = 0.466$, and (right panel) after 2000 shear cycles ($t \approx 10^7$). No indications of anisotropy is observed.
6. Energy barriers

To obtain an estimate of the energy barriers surrounding the low energy minima we investigate the distribution of strain required for the first plastic rearrangement when these configurations are sheared. These strain intervals provide a measure of the potential energy barriers when these configurations are sheared. These strain intervals thus provide a measure of the potential energy barriers surrounding the undeformed inherent structures. For $T = 0.4$, the distributions from MD and cyclic shear are quantitatively the same, whereas they are easily distinguishable from higher temperature MD results.

![Energy barriers distribution](image)

**FIG. A11.** The distribution of the strain intervals ($\Delta \gamma_{iso}$) at which the first plastic deformation event occurs for inherent structures obtained through cyclic shear and from NVT molecular dynamics. The strain interval values are a measure of the energy barriers surrounding the undeformed inherent structures. For $T = 0.4$, the distributions from MD and cyclic shear are quantitatively the same, whereas they are easily distinguishable from higher temperature MD results.

7. Shearing in variable planes

We considered the effect of shearing in alternating shear planes ($xy$, $xz$, and $yz$, repeated after 3 cycles). As shown in Fig. A12 (a) the generated energies are essentially the same (however, it has been reported that for larger systems at lower temperatures and shear amplitudes, alternating shear planes leads to better annealing [37, 67]). In this case also we find the stress anisotropies to be small, and comparable to those of inherent structures quenched directly from liquid configurations, as shown in Fig. A12 (b). Fig. A12 (b) also shows stress anisotropies for shear in a single plane obtained at different shear rates and strain amplitudes, for comparison.

![Stress anisotropies](image)

**FIG. A12.** (a) Inherent structure (IS) energies (when shear is applied in alternating planes) vary in the same way with time as when only $xy$ shear is applied. (c) For strain amplitudes lower than or close to the yielding amplitude, stress anisotropies compare with those of isotropic inherent structures (indicated by the horizontal line) for different strain rates, and for the case when shear in applied in alternating shear planes.

8. Details of Algorithm for Equilibrium Sampling

We provide below details concerning the equilibrium sampling algorithm. Much of these details are standard, and found, e.g. in [61], but they are included here for completeness.

a. Equations of Motion

The dynamics we will consider is the SLLOD dynamics, where the shear is applied through a sinusoidally varying $xy$ strain

$$\gamma_{xy}(t) = \gamma_{max} \sin(\omega t)$$  \hspace{1cm} (2)

which corresponds to a strain rate

$$\dot{\gamma}_{xy} = \gamma_{max} \omega \cos(\omega t).$$  \hspace{1cm} (3)

Nominally we can associate this with a strain rate $\dot{\gamma}_{xy} = \gamma_{max} \omega$ or more precisely, with $\dot{\gamma}_{accum} = 4\dot{\gamma}_{max}$.
The SLLOD equations of motion are written as
\[
\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{r}_i \cdot \nabla \mathbf{v} \tag{4}\]
\[
\dot{\mathbf{p}}_i = \frac{\mathbf{F}_i}{m} - \mathbf{p}_i \cdot \nabla \mathbf{v} - \alpha \mathbf{p}_i \tag{5}\]
With simple \(xy\) shear, we have
\[
\mathbf{r}_i \cdot \nabla \mathbf{v} = \dot{\gamma}_{xy} y_i, \mathbf{i} \tag{6}\]
and the equations of motion in component form are

\[
\begin{align*}
\dot{x}_i &= \frac{p_{x\,i}}{m} + \dot{\gamma}_{xy} y_i \\
\dot{y}_i &= \frac{p_{y\,i}}{m} \\
\dot{z}_i &= \frac{p_{z\,i}}{m} \\
\dot{p}_{x\,i} &= \frac{F_{x\,i}}{m} - \dot{\gamma}_{xy} y_i - \alpha p_{x\,i} \\
\dot{p}_{y\,i} &= \frac{F_{y\,i}}{m} - \alpha p_{y\,i} \\
\dot{p}_{z\,i} &= \frac{F_{z\,i}}{m} - \alpha p_{z\,i}
\end{align*}
\]

We consider two thermostats, the Gaussian isokinetic thermostat and the Nosé-Hoover thermostat. For the Gaussian isokinetic thermostat, the damping coefficient is given by:
\[
\alpha = \sum_i \frac{p_i \cdot (\mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v})}{m_i} \sum_i \frac{p_i^2}{m_i} \tag{6}
\]
The corresponding expression for the Nosé-Hoover thermostat is:
\[
\alpha = \frac{p_\eta}{Q} \tag{7}
\]
where \(p_\eta\) is the momentum associated with the thermostat coordinate \(\eta\) and \(Q\) is the corresponding mass. \(p_\eta\) is governed by
\[
\dot{p}_\eta = \sum_i \frac{p_i^2}{m} + 3Nk_BT \tag{8}
\]

b. Modified Hybrid Monte Carlo Method

We first describe the steps in the standard Monte Carlo scheme, but in the case that the thermostat temperature is different from the sampling temperature. We consider a system that is characterized by a Hamiltonian
\[
H = \sum_i \frac{p_i^2}{2m} + \Phi(x); \quad \Phi(x) = \sum_{i<j} \phi_{ij}(x_{ij}) \tag{9}
\]
where \(x_i, i = 1, \ldots 3N\) refer to the coordinates of \(N\) particles, and \(p_i\) are the corresponding momenta. We wish to generate an equilibrium sampling of coordinates \(x\),
\[
p_{eq}(x)dx = \frac{1}{Z} \exp(-\beta_s \Phi(x))dx \tag{10}
\]
where \(\beta_s = 1/k_BT_s\), where \(T_s\) is the "sampling" temperature, and
\[
Z = \int dx \exp(-\beta_s \Phi(x)). \tag{11}
\]
The Markov transition probability densities \(p_M(x^t \rightarrow x^{t+1})\) need to satisfy detailed balance condition
\[
p(\{x,p\})p_M(x \rightarrow x')dx \cdot dx' = p(\{x',p'\})p_M(x' \rightarrow x)dx \cdot dx'. \tag{12}
\]
Configurations \(x'\) are generated through a molecular dynamics run, starting with initial coordinates \(x\) and momenta generated according to the Maxwell distribution, with a "thermostat" temperature \(T_t = (k_BT_s)^{-1}\) that need not be the same as \(T_s\). The procedure listed below can be verified to obey the detailed balance condition mentioned above [68] for time reversible and phase space volume preserving dynamics:

1. Starting with \(x\), generate momenta with the Maxwell distribution at temperature \(T_t\)
\[
p_C(p) \propto \exp(-\beta_t p^2/2m) \tag{13}
\]
2. Propagate \((x,p)\) using a time reversible, phase space volume preserving dynamics. For the simplest case, the Hamiltonian dynamics with \(H_0\), we have for the probability of generating \((x',p')\) from \((x,p)\)
\[
p_H((x,p) \rightarrow (x',p')) = p_H((x',-p') \rightarrow (x,-p)) \tag{14}
\]
3. Accept \((x',p')\) with probability
\[
p_A((x,p) \rightarrow (x',p')) = \min\{1, \exp(-\beta_s \Delta \Phi) \exp(-\beta_t \Delta K)\} \tag{15}
\]
where \(\Delta \Phi = \Phi(x',p') - \Phi(x,p)\) and \(\Delta K = \sum_i \frac{p_i^2}{2m} - \sum_i \frac{p_i^2}{2m} \).
4. Return to step 1 and generate new momenta regardless of acceptance.

We next consider the case where the dynamics, while time reversible, does not conserve phase space volume, such as the thermostatted SLLOD dynamics we consider here. We consider for concreteness that the dynamics compresses the phase space volume. Thus, a volume we denote by $dx \, dp$ around $(x, p)$ is mapped to a smaller volume $dx' \, dp'$ around $(x', p')$ with a corresponding increase in the phase space density (see below). As a result, considering a distribution of points proportional to the equilibrium probability density, and the standard Metropolis acceptance probability, the net transition probability in the “forward” direction, proportional to

$$\frac{\exp(-\beta \cdot H(x, p))}{Q} \, \min\{1, \exp(-\beta \cdot \Delta H)\} \, dx \, dp,$$

does not balance that in the "reverse" direction,

$$\frac{\exp(-\beta \cdot H(x', -p'))}{Q} \, dx' \, dp' \, \min\{1, \exp(-\beta \cdot [H(x, -p) - H(x', -p')])\}$$

which can be manipulated to write as

$$\frac{\exp(-\beta \cdot H(x, -p))}{Q} \, dx' \, dp' \, \min\{1, \exp(-\beta \cdot \Delta H)\}$$

The ratio of the forward to reverse transition probability is the ratio of phase space volumes which we write as $\frac{dx \, dp}{dx' \, dp'}$. In order to obtain detailed balance, the acceptance probability must be corrected by a compensation factor $C = \frac{dx' \, dp'}{dx \, dp}$, leading to

$$p_A((x, p) \rightarrow (x', p')) = \min\{1, \exp(-\beta \cdot \Delta H) \cdot C\}, \quad (19)$$

which can be verified to obey detailed balance.

c. Compression of phase space volume

The calculation of the correction term $C$ is done here in two ways. First, we consider how the volume element around the initial state point $(x, p)$ is modified by the dynamics. Second, we can alternately consider how the phase space density is modified by the dynamics.

We consider the phase space point $\Gamma = (x, p)$, and write the dynamics governing it as

$$\dot{\Gamma} = G(\Gamma, t) \quad (20)$$

If we now consider a displacement from $\Gamma$, $\delta \Gamma$, the dynamics of the displacement (which we assume is always small) is given by

$$\delta \dot{\Gamma} = T \cdot \delta \Gamma \quad (21)$$

where

$$T = \frac{\partial G}{\partial \Gamma} = \frac{\partial \dot{\Gamma}}{\partial \Gamma} \quad (22)$$

We can define a phase space volume by considering a set of independent $\delta \Gamma_i$, $i = 1, 2, \ldots, 6N$, and obtaining the determinant of the matrix $M = \{\delta \Gamma_1, \delta \Gamma_2, \ldots, \delta \Gamma_{6N}\}$, as discussed in the context of computing Lyapunov exponents. We have

$$\dot{M} = T \cdot M \quad (23)$$

Formally, we can write the solution as

$$M(t) = \exp \left[ \int T(s) ds \right] M(0) \quad (24)$$

To evaluate this, we consider dividing the time interval $[0, t]$ into infinitesimal segments $dt$ within which we treat the matrix $T$ as being constant (we can take the limit of $dt \rightarrow 0$ eventually). With this, we can write

$$M(t) = \Pi_i \exp[T_i \cdot dt] \cdot M(0) \quad (25)$$

We now write the determinant of $M$ as

$$\det (M(t)) = \det (\Pi_i \exp[T_i \cdot dt] \cdot M(0)) \quad (26)$$

$$= (\Pi_i \cdot \det (\exp[T_i \cdot dt])) \times \det (M(0))$$

$$= (\Pi_i \cdot \exp[T \cdot dt_i]) \times \det (M(0))$$
by the corollary to Jacobi’s formula, \( det (exp(A)) = exp(Tr.A) \). Thus,

\[
\det(M(t)) = \exp \left( \sum_i Tr.T_i \, dt \right) \times \det(M(0)) \tag{27}
\]

\[
= \exp \left( \int Tr.T(s) \, dt \right) \times \det(M(0)) ; \quad dt \to 0
\]

We can write \( det(M) = V_{\Gamma} \), the phase space volume. Further, writing \( Tr.T = \frac{\partial}{\partial t} \Gamma \), we have

\[
V_{\Gamma}(t) = \exp \left[ \int \frac{\partial}{\partial t} \Gamma(s) ds \right] \times V_{\Gamma}(0). \tag{28}
\]

The trace of \( T \) integrated over time \( t \) also equals the sum of Lyapunov exponents times \( t \). We will consider later how this quantity can be calculated for specific dynamics.

The compensation factor \( C \) we are after is therefore

\[
C(t) = \exp \left[ \int \Lambda(\Gamma)(s) ds \right] \tag{29}
\]

where \( \Lambda(\Gamma) = \frac{\partial}{\partial t} \Gamma \) is called the phase space compression factor.

We can alternately consider the time evolution of the phase space density \( f(\Gamma(t), t) \), and the phase space compression is given by \( f(\Gamma, 0)/f(\Gamma, t) \). Considering an ensemble of phase space points, and writing

\[
f(\Gamma, t) = \sum_i \delta(\Gamma - \Gamma_i(t)), \tag{30}
\]

we have

\[
\frac{df(\Gamma, t)}{dt} = \dot{\Gamma} \cdot \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \Gamma} \frac{\partial \Gamma}{\partial t} \tag{31}
\]

\[
= \dot{\Gamma} \cdot \frac{\partial f}{\partial t} - \frac{\partial f}{\partial \Gamma} \left( \dot{\Gamma} f \right) \tag{32}
\]

\[
= -f \frac{\partial}{\partial t} \dot{\Gamma} \tag{33}
\]

\[
= -f \Lambda(\Gamma) \tag{34}
\]

which we see leads to the same result as before. \( \Lambda(\Gamma) \) can be written in more explicit notation as

\[
\Lambda(\Gamma) = \sum_{i=1}^{3N} \left( \frac{\partial}{\partial \dot{q}_i} , \frac{\partial}{\partial p_i} \right) \cdot (\dot{q}_i, \dot{p}_i). \tag{35}
\]

Considering the SLLOD equations of motion with Gaussian thermostat, we can compute \( \Lambda(\Gamma) \) by using expressions for \( \dot{q}_i \) and \( \dot{p}_i \), and obtain

\[
\Lambda(\Gamma) = N(\nabla \cdot v - \nabla \cdot v - 3\alpha) = -3N\alpha \tag{36}
\]

ignoring terms of \( O(1) \) that arise from differentiating \( \alpha \), which are proportional to \( \alpha \) and the strain rate. For SLLOD dynamics without thermostating, the phase space compression factor is zero, and therefore phase space volume is conserved, even though the dynamics is non-Hamiltonian. Thus, the standard HMC can be used if we don’t apply a thermostat. With the thermostat, the damping coefficient \( \alpha \) allows computation of the correction factor \( C \) needed for the modified HMC.

d. Work done and heat dissipation

We finally consider the time derivative of the internal energy of the system in order to obtain expressions for the rate of work done and the rate of heat change (or dissipation), which enables us to relate the compensation factor \( C \) to heat.

To understand how the internal energy changes can be related to \( \Lambda \) consider the following:

\[
H = K + \Phi \tag{37}
\]

where \( H \) is the total internal energy, \( K \) is the thermal (kinetic) energy and \( \Phi \) is the internal (pairwise) potential energy.

\[
K = \sum_{i=1}^{N} \frac{p_i \cdot p_i}{2m_i} \tag{38}
\]

\[
\Phi = \frac{1}{2} \sum_{i,j}^{N} \sum_{i \neq j} \phi_{ij}(r_{ij}) \tag{39}
\]

The rate of change of energy is then

\[
\frac{dH}{dt} = \frac{dK}{dt} + \frac{d\Phi}{dt} \tag{40}
\]

We find

\[
\frac{dK}{dt} = \sum_{i=1}^{N} \frac{p_i \cdot \dot{p}_i}{m} \tag{41}
\]

\[
= \sum_{i=1}^{N} \frac{p_i}{m} \cdot (F_i - p_i \cdot \nabla v - \alpha p_i) \]

\[
= \sum_{i=1}^{N} \frac{p_i}{m} \cdot F_i - \sum_{i=1}^{N} \frac{p_i p_i}{m} : \nabla v - \alpha \sum_{i=1}^{N} \frac{p_i^2}{m}
\]
\[ \frac{d\Phi}{dt} = \sum_i \nabla_i \Phi \cdot \dot{r}_i \]  
\[ = - \sum_i F_i \cdot \left( \frac{p_i}{m_i} + r_i \nabla v \right) \]  
\[ = - \sum_{i=1}^N \frac{p_i}{m_i} \cdot F_i - \sum_{i=1}^N (r_i F_i)^T : \nabla v \]  
\[ = - \sum_{i=1}^N \frac{p_i}{m_i} \cdot F_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (r_{ij} F_{ij})^T : \nabla v \]  
\[ (42) \]
\[ (43) \]
\[ (44) \]
\[ (45) \]

(NB: The time dependence of \( \nabla v \) does not enter and make a difference to these equations.) Combining the two terms, we have

\[ \frac{dH}{dt} = - \sum_{i=1}^N \frac{p_i p_i}{m_i} : \nabla v - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (r_{ij} F_{ij})^T : \nabla v - \alpha \sum_{i=1}^N \frac{p_i \cdot p_i}{m_i} \]  
\[ = -V \sigma^T : \nabla v - \alpha \sum_{i=1}^N \frac{p_i \cdot p_i}{m_i} \]  
\[ (46) \]
\[ (47) \]

We have the pressure tensor defined as

\[ \mathbf{P} = 1 \left[ \sum_{i=1}^N \frac{p_i p_i}{m_i} + \sum_{i=1}^N r_i F_i \right] \]  
\[ (48) \]

The stress tensor \( \sigma \) is defined as the negative of the pressure tensor \( \sigma = -\mathbf{P} \). For strain rate in the \( xy \) plane with only \( \frac{\partial v_x}{\partial y} \neq 0 \), we have

\[ \frac{dH}{dt} = - \sum_{i=1}^N \left[ \frac{p_{xi} p_{yi}}{m} + F_{x i y i} \right] \dot{\gamma}_{xy} - \alpha \sum_{i=1}^N \frac{p_i^2}{m} \]  
\[ = -V \sigma_{xy}^T \dot{\gamma}_{xy} - \alpha \sum_{i=1}^N \frac{p_i^2}{m} \]  
\[ (49) \]
\[ (50) \]

Using \( \sum_{i=1}^N \frac{p_i^2}{m} = 3Nk_BT \), we have

\[ \frac{dH}{dt} = - \sum_{i=1}^N \left[ \frac{p_{xi} p_{yi}}{m} + F_{x i y i} \right] \dot{\gamma}_{xy} - 3N\alpha k_BT \]  
\[ = -V \sigma_{xy}^T \dot{\gamma}_{xy} - 3N\alpha k_BT \]  
\[ = V \sigma_{xy}^T \dot{\gamma}_{xy} + \Lambda k_BT \]  
\[ (51) \]
\[ (52) \]
\[ (53) \]
\[ (54) \]

A change in energy over some interval \( t \) is given by

\[ \Delta H(t) = \int_0^t V \sigma^T(s)_{xy} \dot{\gamma}_{xy}(s) ds + k_BT \int_0^t \Lambda(s) ds \]  
\[ = \Delta W + \Delta Q \]  
\[ (55) \]
\[ (56) \]

Based on the above, the multiplicative factor in the Monte Carlo step for thermostatted systems discussed
above will be

\[ C = \exp \left( \int \Lambda(s) ds \right) = e^{\Delta Q / T} \]  \hspace{1cm} (57) \]

\[ p_A((x, p) \rightarrow (x', p')) = \min \{ 1, \exp(-\beta_s \Delta H) \exp(\beta_s \Delta Q) \} \]
\[ = \min \{ 1, \exp(-\beta_s (\Delta H - \Delta Q)) \} \]  \hspace{1cm} (58)
\[ = \min \{ 1, \exp(-\beta_s \Delta W) \}. \]  \hspace{1cm} (59)

When the system and thermostat temperatures are not the same, we have

\[ p_A((x, p) \rightarrow (x', p')) = \min \{ 1, \exp(-\beta_s \Delta \Phi) \exp(-\beta_i \Delta K) \exp(\beta_i \Delta Q) \} \]  \hspace{1cm} (60)

With the expressions above for \( \Delta W \), \( \Delta Q \) given above (Eq. 56), Eqs. 60 and 61 provide the acceptance probabilities for an equilibrium sampling algorithm.

9. Additional Results from Equilibrium Sampling

Monte Carlo Simulations

As noticed in previous work \cite{59}, the model studied here, the Kob-Andersen binary mixture, crystallizes on time scales that are accessible to long molecular dynamics simulations. In particular, at \( T = 0.4 \), for \( N = 4000 \), results in \cite{59} indicate that the crystallization time \( \tau_X \sim 100 \tau_x \). With \( \tau_x \sim 1.5 \times 10^6 \) at this temperature, we do indeed see crystallization on the expected time scale, but on the lower side by a factor of 2. We analyse the crystallization kinetics employing standard methods \cite{59,60} that are based on defining bond orientational order parameters for each particle \( i \), \( q_{ij}(i) = \frac{1}{n_i} \sum_{j=1}^{n_i} Y_{ij} \cos(\theta_{ij}, \phi_{ij}) \), where \( \theta_{ij} \) and \( \phi_{ij} \) are angles formed by separation vectors \( r_{ij} \) between particles \( i \) and neighbors \( j \) in the laboratory frame. The \( l \) value used is 6. We employ cutoffs for defining neighbors from the location of the first minimum of the pair correlation functions \( g_{ij}(r) \), which are, \( r_{\text{cut}} = 1.4 \), \( r_{\text{cut}}^{AB} = 1.25 \) and \( r_{\text{cut}}^{BB} = 1.1 \). Following \cite{59}, we define two neighbors to be bonded if the normalised dot product \( q_{ij}(i)q_{ij}(j)/|q_{ij}(i)||q_{ij}(j)| \) is bigger than 0.7, and a particle is labeled as crystalline if it has at least 7 such bonds. Crystalline particles are then connected if they are within a cutoff distance, for which we use slightly larger values \( r_{\text{clust}} = 1.5 \), \( r_{AB}^{\text{clust}} = 1.4 \) and \( r_{BB}^{\text{clust}} = 1.2 \). We then perform a cluster finding procedure to identify all clusters of connected crystalline particles and report the largest cluster size of crystalline particles. Because the largest cluster size may not fully reflect the degree of crystallinity in cases where the cluster sizes are small, and the clustering definition may not capture physical proximity, we also report the total number of crystalline particles. These are shown in Fig. A13 for one trajectory each with \( T = 0.4 \) and \( T = 0.37 \), both without Monte Carlo sampling between cycles and with sampling. For \( T = 0.4 \) (Fig. A13 (a)), the largest cluster grows significantly beyond time \( t \sim 7.5 \times 10^6 \) reaching large values. For the other cases, the degree of crystallinity is never very large, but for \( T = 0.37 \) (Fig. A13 (c)), beyond time
$t \sim 4.5 \times 10^6$, there is a rise in the number of crystalline particles. In [59], the critical nucleus size is estimated to be $50 - 100$ particles. In our analysis, when a trajectory exhibits persistently a largest crystalline cluster size of 30 or above, or the total number of crystalline particles is above 60 in a persistent fashion, or even otherwise, when the growth of crystallinity suggests the onset of crystallization, we exclude the corresponding trajectory segments (i.e., parts of the trajectory thereafter) from the computation of averages and statistics. Thus, for example, for the trajectory shown in Fig. A13 (a), we do not consider the trajectory after $t \sim 7.5 \times 10^6$, and for the trajectory shown in Fig. A13 (c), we do not consider the trajectory after $t \sim 4.5 \times 10^6$. All the data in Fig. A13 (b) and (d) are included in the analysis.

![Histograms of inherent structure energies obtained without (SLLOD) and with (SLLOD/MC) equilibrium Monte Carlo sampling, demonstrating that without Monte Carlo sampling, the energies are shifted to higher values compared to the expected equilibrium values, whereas with Monte Carlo sampling, they are close to the expected equilibrium values.](image1)

**FIG. A14.** Histograms of inherent structure energies obtained without (SLLOD) and with (SLLOD/MC) equilibrium Monte Carlo sampling, demonstrating that without Monte Carlo sampling, the energies are shifted to higher values compared to the expected equilibrium values, whereas with Monte Carlo sampling, they are close to the expected equilibrium values.

**b. Proper sampling under large amplitude shear:**

Although results from cyclic shear without Monte Carlo sampling shown in the main text are close to those obtained from equilibrium Monte Carlo sampling, this is not guaranteed and is not always the case. We have shown above that with an increase in strain amplitude, the inherent structure energies attained increase beyond the optimal amplitude. In such a case, we should expect that the energy distribution obtained without equilibrium Monte Carlo sampling will deviate from that obtained with such sampling, which should generate an equilibrium ensemble. We demonstrate here that such is indeed the case. However, with an increase in strain amplitude (and/or system size; see below), we expect that the acceptance rate of the Monte Carlo procedure may also decrease, and sampling will be less efficient. Nevertheless, we should expect to converge to the correct distribution of energies. In order to demonstrate this, we consider a system of $N = 500$ particles, simulated at $T = 0.4$, at a large strain amplitude of $\gamma_{\max} = 0.03$. We generate 5 independent trajectories of length $t = 9.42 \times 10^6$ without Monte Carlo sampling, and 10 independent trajectories of length $t = 1.88 \times 10^7$ with Monte Carlo sampling and obtain the histogram of energies in each case by averaging over the independent runs. Results shown in Fig. A14 do indeed confirm that the Monte Carlo procedure generates a distribution of energies with a mean that is close to the expected equilibrium value (in this case, by extrapolation, $e_{IS} = -7.028$, based on results for $N = 1000$ described above) whereas without Monte Carlo sampling, the energies are clearly higher. We note in passing that there appears to be a small shift in energies to higher values with a decrease in system size but do not analyse such system size dependence further.

![The histogram of work done during a cycle for cyclic shear runs with $T = 0.3$, for (a) $N = 4000$, $\gamma_{\max} = 0.03$, (b) $N = 500$, $\gamma_{\max} = 0.03$, (c) $N = 4000$, $\gamma_{\max} = 0.03$, where shear is applied to a subvolume of $\approx 500$ particles (SS), and (d) $N = 4000$, with adaptive tuning of $\gamma_{\max}$ (here, on average (A), $\gamma_{\max} = 0.004$).](image2)

**FIG. A15.** The histogram of work done during a cycle for cyclic shear runs with $T = 0.3$, for (a) $N = 4000$, $\gamma_{\max} = 0.03$, (b) $N = 500$, $\gamma_{\max} = 0.03$, (c) $N = 4000$, $\gamma_{\max} = 0.03$, where shear is applied to a subvolume of $\approx 500$ particles (SS), and (d) $N = 4000$, with adaptive tuning of $\gamma_{\max}$ (here, on average (A), $\gamma_{\max} = 0.004$).

**c. Work Done:**

The work done over a cycle depends on the system size $N$ and the strain amplitude $\gamma_{\max}$, among other variables. For $N = 4000$, with $\gamma_{\max} = 0.03$, the histogram work done is shown in Fig. A15. The average value is about 2, with makes the acceptance probabilities of Monte Carlo moves negligible. For $N = 500$, with $\gamma_{\max} = 0.03$, the
distribution of values is nearly centered around zero. Also shown are the histograms of work done for $N = 4000$, $\gamma_{\max} = 0.03$, when only a subvolume of $\approx 500$ particles is sheared (labeled SS), and for $N = 4000$, when the $\gamma_{\max}$ is varied adaptively to ensure a specified acceptance probability (labeled A). In the case shown, the the average values of $\gamma_{\max} \approx 0.004$. In all cases, cyclic shear is applied without Monte Carlo rejection, with $T_s = T_t = 0.3$.

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