Isomorphs in sheared binary Lennard-Jones glass: Transient response

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We have studied shear deformation of binary Lennard-Jones glasses to investigate the extent to which the transient part of the stress strain curves is invariant when the thermodynamic state point is varied along an isomorph. Shear deformations were carried out on glass samples of varying stability, determined by cooling rate, and at varying strain rates, at a state point deep in the glass. Density changes up to and exceeding a factor of two were made. We investigated several different methods for generating isomorphs but none of the previously developed methods could generate sufficiently precise isomorphs given the large density changes and non-equilibrium situation. Instead, the temperatures for these higher densities were chosen to give state points isomorphic to the starting state point by requiring the steady state flow stress for isomorphic state points to be invariant in reduced units. In contrast to the steady state flow stress, we find that the peak stress on the stress strain curve is not invariant. The peak stress decreases by a few percent for each ten percent increase in density, although the differences decrease with increasing density. Analysis of strain profiles and non-affine motion during the transient phase suggests that the root of the changes in peak stress is a varying tendency to form shear bands, with the largest tendency occurring at the lowest densities. We argue that this reflects the effective steepness of the potential; a higher effective steepness gives a greater tendency to form shear bands.

I. INTRODUCTION

In recent years it has been realized that many model systems for simulating liquids and glasses have a hidden scale invariance, as a consequence of which curves in the phase diagram can be identified along which many structural and dynamical properties are invariant when expressed in an appropriate scaled-unit system. These curves are called isomorphs [1]. Isomorphs have been studied extensively using computer simulations [1–5] of many different model systems [6–7], and experimental consequences have also been tested [8–9]. Reviews of the overall theoretical framework and the many interesting consequences arising from its basic assumptions can be found in Refs. [10–12]. An example of the use of isomorph concept as a theoretical tool is a method for efficient calculation of melting curves [13–14].

More recently, the consequences of hidden scale invariance in non-equilibrium situations, especially aging, have begun to be studied [15]. An important class of non-equilibrium phenomena involves shear deformation and plastic flow. The first study of isomorphs in a sheared system was already in 2013, where the single-component Lennard-Jones fluid and the Kob-Andersen binary fluid [16–18] were studied in planar Couette flow in steady-state conditions [19]. In 2019 we published work studying deformation of Kob-Andersen glasses under steady state flow with relatively modest density changes, up to 10% [20]. There we studied the statistics of the steady state rheology: the (mean) flow stress, its standard deviation, fluctuations and autocorrelation, as well as distributions of stress changes over small strain intervals, at varying strain rates.

The aim of the present work is to study isomorphs in a true out-of-equilibrium context, focussing on the transient behavior of sheared glasses, specifically the initial part of the stress strain curve, characterized by an (approximately) linear stress rise corresponding to (approximately) elastic behavior, followed by a stress peak, and then relaxation towards the steady state. While we are interested in investigating to what extent the entire stress-strain curve collapses along a given isomorph (with given cooling and strain rates), the discussion will focus particularly on the peak stress in the transient phase, and the flow stress for comparison. These two quantities (in reduced form) are convenient to plot as a function of density along isomorphs, giving a quick overview of the degree of invariance. We are also interested in attempting larger density changes than before. The model studied is the usual Kob-Andersen binary Lennard-Jones system [16–18].

For the prior work on the steady-state behavior the main thermodynamic parameters were density, temperature and strain rate. Since the first two were linked along an isomorph, there were effectively two parameters: a parameter labelling the isomorph (in principle the excess entropy, but numerical values for this are hard to obtain), and the reduced-unit strain rate. A feature of the transient state regime is that the thermal history of the glass prior to deformation becomes relevant. Our glasses are prepared by cooling at a fixed cooling rate, from a temperature near the melting point at the lowest density considered. Each deformation simulation is thus characterized by four parameters: the density $\rho$, temperature $T$,
$T$, cooling rate $R_{c,0}$ and strain rate $\dot{\epsilon}$. Since we focus on trying to identify isomorphs, density and temperature are varied according to the (putative) isomorph, and cooling rate always refers to the initial (low) density in real units (hence the subscript 0), while strain rate is referred to using reduced units (see Sec II A) isomorph invariance can only be expected when the strain rate is fixed in reduced units). For shearing simulations at densities higher than that of the cooling runs, configurations were scaled uniformly to the desired density (after cooling but before shearing) and the kinetic energy set to that appropriate for the corresponding (isomorphic) temperature. In this way the thermal histories of starting configurations at different points along the isomorph are identical by construction.

We focus on two questions. First, how can one reliably and efficiently identify isomorphs spanning large density changes in far-from-equilibrium systems? Second, to what extent is the transient behavior observed in the transition from unsheared to steady-state flow isomorph invariant? The behavior in question includes both the peak observed in the stress-strain curve and analysis of displacement profiles in terms on inhomogeneous strain. The first question is central when studying isomorphs and can be more precisely phrased as: Given a change of density, what is corresponding temperature change that gives essentially invariant behavior? We review below several procedures based on analysis of equilibrium fluctuations of the potential energy $U$, and the virial $W$ (the part of the pressure associated with interactions, apart from a factor of volume). A more recent method based on analysis of how particle forces change when a configuration is uniformly scaled to a different density [21] is also considered; this method does not require equilibrium sampling and is therefore promising for the non-equilibrium situations we are interested in. We find that none of these methods is sufficiently accurate for our purposes, and adopt an operational definition of isomorphs in terms of matching flow stress. In the second half of the paper, having applied this operational definition, which allows us to collapse the steady-state behavior over large density changes, we focus on the second question and study the initial peak in the stress strain curve. The main result here is that the peaks do not collapse and that this failure to collapse seems to be due to a varying tendency for shear-banding along the proposed isomorph.

II. ISOMORPH THEORY ESSENTIALS

A. Reduced units

The heart of the existence of isomorphs is that a phase space trajectory at one density and temperature can be scaled to another density (corresponding to a scaling of space) and another temperature (corresponding to a scaling of time, and thereby velocities and kinetic energy) and be, in fact, a valid trajectory at the new state point. Alternatively, trajectories can be found at the two isomorphic state points which are identical apart from rescaling space and time, and equally probable in their respective ensembles. This means considering the reduced position coordinates $\tilde{\mathbf{r}}_i \equiv \rho^{1/3}\mathbf{r}_i$; i.e., scaling essentially by the average interparticle spacing, using $\rho = N/V$, the number density of the system with $N$ particles in a volume $V$. The reduced time is $\tilde{t} = t\rho^{1/3}\sqrt{k_B T/\langle m \rangle}$; i.e., scaling essentially by the time for a particle with the mean mass $\langle m \rangle$ to cross an interparticle spacing with the thermal velocity. This is sometimes called the “same movie” principle. It follows that a correct comparison of isomorphic trajectories involves putting all quantities into dimensionless form, called “putting into reduced units,” by scaling lengths and times as above, and consistent with these, energies by $k_B T$. Masses are simply scaled by the average particle mass (a non-dynamical, non-thermodynamic quantity, which in our model is set to unity anyway). The scaling for all other quantities can be derived from these $[\Pi]$. As an example the flow stress, having units of energy density, has the reduced form

$$\tilde{\sigma}_f \equiv \frac{\sigma_f}{\rho k_B T}.$$  

(1)

B. Methods for identifying isomorphs in equilibrium

There are several methods currently in use for identifying isomorphs in equilibrium. That is, taking a configuration at $(\rho_1, T_1)$ and identifying other parameters $(\rho_2, T_2)$ that are isomorphic. We briefly introduce these methods here for two reasons. Firstly, to set the stage for our work extending these methods to the out-of-equilibrium systems of interest (discussed in Sec. V). Secondly, because we will use the analytic method (Sec II B 4) to interpolate our isomorph curve in our out-of-equilibrium systems.

1. Integration using the density scaling exponent $\gamma$

In equilibrium the slope of isomorphs in the $\ln \rho, \ln T$ plane is given by the so-called density scaling exponent $\gamma$, defined generally as the slope of configurational adiabats—curves along which the excess entropy is constant $[\Pi]$:

$$\left( \frac{\partial T}{\partial \rho} \right)_{S_{ex}} = \gamma(\rho, T) = \frac{\langle \Delta U \Delta W \rangle}{\langle (\Delta U)^2 \rangle}$$  

(2)

where the second equality indicates how $\gamma$ is determined from fluctuations at a particular state point. Angle brackets represent NVT ensemble averages, and the last expression is simply the linear regression slope of a scatter plot of $W$ against $U$. The virial $W$ can be defined as the derivative of $U$ for a configuration with respect to
In $\rho$, where $\rho \equiv N/V$ is the number density of the system. When taking the derivative it should be understood that the number and relative positions of the particles are kept fixed and only a uniform scaling is involved. Thus $W$ contains information about how the potential energy surface changes under (infinitesimal) uniform scaling and therefore is naturally relevant for the identification of isomorphs. From the same linear regression fit a correlation coefficient $R$ may be extracted, which is used to gauge the expected quality of the isomorphs. By determining $\gamma$ from fluctuations an isomorph in equilibrium may be traced by simple numerical integration (explicit Euler method) of Eq. (2), taking small steps in density (typically 1%, although larger jumps are possible with higher order integration techniques). For systems with interactions described by an inverse power law (IPL) with a particular exponent $n$, exact isomorphs exist with the density scaling exponent is $n/3$: otherwise it depends mainly on density, though it does have some temperature dependence.

2. Direct isomorph check

An early formulation of isomorphism involves the proportionality of Boltzmann factors of corresponding microscopic states. Here “corresponding” means all particles being the same in reduced coordinates, i.e., one configuration is obtained from the other by a uniform scaling. A consequence of this proportionality, obtained simply by taking logarithms, is a proportionality between scaled and unscaled potential energies

$$U_f(R_f) = \frac{T_f}{T_i} U_i(R_i) + \text{const.}, \quad (3)$$

where subscripts $i$ and $f$ indicate potential energies evaluated at initial and final densities, respectively, for any configuration with given reduced coordinates. Here we use the upper case boldface $R$ to represent the entire $3N$-vector of particle coordinates, for convenience, and the equality of scaled coordinates can be expressed as $\tilde{R}_f \equiv \rho_f^{1/3} R_f = \rho_i^{1/3} R_i \equiv \tilde{R}_i$. Eq. (3) was originally considered a simple check of the basic isomorph concept of proportional energy fluctuations, hence the name direct isomorph check (DIC)\cite{1}, but it also suggests a method for identifying isomorphs: Given densities $\rho_i$ and $\rho_f$, and the temperature $T_i$, the temperature $T_f$ such that state point $\rho_f, T_f$ is isomorphic to state point $\rho_i, T_i$ may be identified by (1) sampling configurations from an equilibrium simulation at $\rho_i, T_i$, (2) scaling them to density $\rho_f$, (3) calculating the potential energies of the scaled configurations, and (4) making a scatter plot of the scaled versus unscaled potential energies. Without requiring proportionality of Boltzmann factors one can also derive the DIC by considering configurational adiabats\cite{22}. Furthermore, when considering infinitesimal density changes the DIC reduces to the method of integrating Eq. (2).

3. Stress-based direct isomorph check

One can interpret the DIC as choosing the temperature $T_2$ by requiring the reduced-unit energy fluctuations to be as close as possible between the two state points, where “as close as possible” involves a linear regression fit. One can in principle make a similar requirement for other quantities, for example the virial, whose fluctuations should also be related by being the same in reduced units. Or indeed the shear stress (configurational part). The latter leads to an alternative version of the direct isomorph check where the (configurational part of) the shear stress for scaled configurations is plotted against that for the unscaled ones. In this case, in view of Eq. (1), the slope of the linear regression should be $\rho_f T_f / \rho_i T_i$. This suggests an alternative method for identifying an isomorphic temperature which may be relevant in deformation simulations. The shear stress given by our code includes the (small) kinetic part by default; we have checked in one case that its presence make a negligible difference to the fitted slope.

4. Analytic isomorph formula for LJ potentials

For pair potentials an analytic formula describing the shapes of isomorphs is available\cite{23, 24}, which for the Lennard-Jones potential takes the form $T(\rho) \propto h(\rho)$, where the density scaling function $h(\rho)$ is given by

$$h(\rho) = A \rho^4 - B \rho^2 \quad (4)$$

The analytic form of $h(\rho)$ is directly related to that of the potential (indeed it is essentially the second derivative of the pair potential, evaluated at $r = \rho^{-1/3}$ and expressed in reduced units)\cite{25}. The overall normalization of $h(\rho)$ is undefined since there is a proportionality constant in the relation between it and the temperature, so there is in fact only one free parameter, which can be taken to be the ratio $B/A$. If this is known then given two densities, $\rho_i$ and $\rho_f$, and a temperature $T_i$ corresponding to density $\rho_i$, the temperature $T_f$ corresponding to density $\rho_f$ is given by

$$T_f = T_i \frac{h(\rho_f)}{h(\rho_i)} = T_i \frac{\rho_i^4 - (B/A) \rho_i^2}{\rho_f^4 - (B/A) \rho_f^2} \quad (5)$$

To fix the parameter $B/A$ two options are available. One can note that the logarithmic derivative of $h(\rho)$ must also be equal to the density scaling exponent $\gamma$,

$$\gamma(\rho) = \frac{d \ln h(\rho)}{d \ln \rho} = \frac{4 \rho^2 - 2(B/A) \rho^2}{\rho^2 - (B/A) \rho^2}, \quad (6)$$

where we assume explicitly that $\gamma$ depends only on density. Considering a particular reference density $\rho_{\text{ref}}$ at
which $\gamma$ is to be evaluated (for example by simulation), isolating $B/A$ gives

$$\frac{B}{A} = \frac{(\gamma(\rho_{\text{ref}}) - 4)\rho_{\text{ref}}^2}{(\gamma(\rho_{\text{ref}}) - 2)}$$

In principle, if isomorph theory was exact, one could run a single simulation at the reference density, evaluate $\gamma$ from the $U, W$ fluctuations there, use Eq. (7) to determine $B/A$ and generate the whole isomorph using Eq. (5). This works reasonably well for small density jumps, say 10%—so certainly better than integration method with steps of 1%—but it does not give accurate temperatures for very large density jumps. Rather, the greatest utility of the analytic isomorph expression is its use in interpolating between points known to be isomorphic to get the points between [26]. That is, if both densities and temperatures for two state points, $\rho_i, T_i$ and $\rho_f, T_f$ are known, Eq. (5) can be solved for $B/A$, giving

$$\frac{B}{A} = \frac{\rho_i^4 - \rho_i^4 T_i}{\rho_f^4 - \rho_f^4 T_f}$$

Then isomorphic temperatures for densities between $\rho_i$ and $\rho_f$ can readily be found using Eq. (5) (replacing $\rho_f$ and $T_f$ with the intermediate values). This is the manner in which we use the analytical formula in this work—note that it does not explicitly depend on having equilibrium.

### III. MODELS, STARTING PARAMETERS, BASIC PROCEDURES

In this section we give a brief overview of the model we use, how we cool, and how we deform. We work with the standard Kob-Andersen 80-20 binary Lennard-Jones system with the only slight difference being that we use a shifted-force cutoff [27]. This is imposed at distance 2.5 $\sigma$ for each interaction type. When expressing in ordinary (non-reduced) units we use the unit system defined by the energy parameter of the AA interaction, $\epsilon_{AA}$, the length parameter of the AA interaction, $\sigma_{AA}$, and the particle mass (common to both A and B particles). For brevity we refer to these as “Lennard-Jones” units. A challenge with investigating the transient part of the stress and strain curve is that the fluctuations cannot just be averaged out by running longer. Considering the example shown in Fig. 1 we note that the fluctuations in panel (a) of are quite severe and avalanche like, even though the temperature is not as low as in our last paper [20]. To manage the fluctuations we use fairly large system sizes ($N = 100000$) and multiple independent runs, starting from an ensemble of configurations generated by separate cooling runs. There are 40 members in this ensemble. Studying the run-to-run deviations also allows us to determine errors on flow stress and peak stress quite precisely.

### A. Cooling

The lowest density we consider is 1.183, which is close to the density 1.2 studied by Kob and Andersen and most often by others. At this density we run a liquid simulation involving $N = 10000$ particles at the relatively high temperature of 1.0 (known to be close to the melting temperature for this composition [28]). Forty independent configurations were sampled from this NVT run and used as the start of the cooling runs. We have cooled at rates $10^{-5}$, $10^{-6}$, and $10^{-7}$ in Lennard-Jones units down to temperature 0.3, deep in the glassy state. The cooling is done at constant $V$ (constant density).

### B. Shear deformation

For shear deformation simulations we employ the SLLOD [24, 30] equations of motion and Lees-Edwards boundary conditions [31, 32]. The direction of shearing is the $x$-direction with the gradient in the $y$-direction, therefore the relevant component of stress is $xy$. As is common in SLLOD-based simulations the temperature is controlled using an isokinetic thermostat, which maintains a fixed kinetic energy, chosen to be $3(N - 1)k_BT$. We choose the shear rate to be fixed in reduced units (essential for correct comparison of isomorph invariant quantities along isomorphs) to the value $10^{-3}$, $10^{-4}$, or $10^{-5}$. We also choose the time step to be fixed in reduced units, which is practical—it automatically ensures that a time step which is stable at one density and temperature will be stable along the isomorph. We choose a real time step of 0.004 (LJ units) at the lowest density 1.183 and temperature 0.3; thus the real time step is smaller at higher densities and temperatures, proportional to $\rho^{-1/3}T^{-1/2}$.

In the following it turns out best to use the flow stress, defined as the mean stress during the steady state regime, to determine isomorphs. For this purpose we define strains greater than 2 (200%) as the steady state for all shear simulations. This choice originates from inspection of the potential energy versus strain curve; we find that the potential energy of the slowest cooled configuration under slowest shear gradually reaches the steady state value at a strain between 1 to 2, see Fig. 1 (and also Fig. 3), which shows examples of stress-strain curves and potential energy-strain curves. In this case the cooling rate for the glasses was $10^{-7}$ in LJ units and the reduced shear rate was $10^{-5}$, corresponding to a real shear rate of about $5.8 \times 10^{-6}$. By eye the shear stress seems to be essentially at its steady-state value by strain 0.5, but for this slowly cooled system the potential energy has not converged to the steady-state value until around strain 2.0 [33].

We need to analyze the stress and strain data to extract mean values as well as uncertainties, so it is worth briefly giving the details of these calculations. Given the many independent runs, the total strain for each shear-
ing run can be relatively modest, specifically 4 (400%), of which the last 200% is used for determining the flow stress. We find the mean reduced stress in this steady state strain regime for each shear simulation, giving 40 independent estimates. We then use the average of 40 shear runs as the flow stress at the corresponding density, temperature, strain rate, and cooling rate. Error bars are computed using the usual formula for the standard error on the mean[34]: dividing the sample standard deviation of the 40 data points by \( \sqrt{40} \). For the stress peak height (preceding the steady state), each individual stress-strain curve is too noisy to determine accurate values; accordingly, we take the 40 independent runs and average them 8 at a time to give five independent stress-strain curves. We then find the peak stress height for one curve by fitting the region of the averaged stress-strain curve around the peak to a fourth-degree polynomial. The interval for fitting is the strain with the numerically largest shear stress, plus or minus 0.05. Taking these five groups each averaged over 8 simulations, we average those five stress peak values to define the measured peak stress height. The uncertainty of this value is then the sample standard deviation of the 5 estimates divided by \( \sqrt{5} \).

FIG. 1: Examples of reduced-unit shear stress (top panels) and potential energy per particle (bottom panels) versus strain, from shear deformation of a binary Lennard-Jones glass with density 1.183 at temperature 0.3. The glass was prepared by cooling at the rate \( 10^{-6} \) (LJ units), while the deformation was carried out at reduced strain rate \( 10^{-5} \), meaning the real strain rate was \( 10^{-5} \rho^{1/3}(T)^{1/2} \approx 5.8 \times 10^{-6} \). The left panels show curves from a single run, while the right panels show the average of 40 independent runs.

IV. EFFECTS OF STRAIN RATE AND COOLING RATE

Here to set the stage we show flow stress and peak stress at starting state point for different strain rates and cooling rates. In this section we do not consider isomorphs and restrict attention to a single density-

temperature state point, namely \( \rho_0 = 1.183, T = 0.3 \) which in the following will be our initial, or reference state point for constructing isomorphs.

FIG. 2: Reduced peak stress \( \bar{\sigma}_p \) and flow stress \( \bar{\sigma}_f \) as function of reduced strain rate \( \bar{\epsilon} \) (a,c) and cooling rate \( R_{c,0} \) (b,d). Black, red, and blue are for \( R_{c,0} = 10^{-5}, 10^{-6}, 10^{-7} \); sphere, square, and up triangle are for \( \bar{\epsilon} = 10^{-3}, 10^{-4}, 10^{-5} \). The flow stress \( \bar{\sigma}_f \) is within errors independent of \( R_{c,0} \) but increases with \( \bar{\epsilon} \). See the text for a discussion of the uncertainties of these measurements, which for these data are smaller than the symbol size. The three horizontal lines in panel (d) are the average of the corresponding three points of the same \( \bar{\epsilon} \).

FIG. 3: Reduced potential energy against strain sheared with \( \bar{\epsilon} = 10^{-3}, 10^{-5} \) for the three cooling rates \( R_{c,0} = 10^{-5} \) (blue and orange), \( 10^{-6} \) (green and red), \( 10^{-7} \) (purple and brown) at \( \rho = 1.183 \) and \( T = 0.3 \). Each curve is an average of 40 simulations.

Since we do not expect perfect isomorphs, both because isomorphs are never perfect, especially over large density changes, and because the intrinsic fluctuations in the stress can obscure the degree of collapse, we need to be able to compare “approximate invariance” with the variation observed when non-isomorphic changes of parameters are considered. In equilibrium situations one can, for example, vary the temperature and density separately while keeping the other fixed. In the
non-equilibrium case more interesting possibilities arise, namely varying the cooling and strain rates. To show how much variation in rheological properties results from varying these rates we plot the peak and flow stresses in Fig. 2 first as a function of strain rate for different cooling rates, and then as a function of cooling rate for different strain rates. It can be seen that an order of magnitude increase in strain rate increases the peak stress by 25-30% [panel (a)] and the flow stress by 5-15% [panel (c)] while an order of magnitude increase in cooling rate decreases the peak stress also 15-20% [panel (b)] but has no effect on the flow stress [panel (d)]. These dependencies are expected in glassy rheology [35]. In particular a lower cooling rate generates a more stable glass, which requires a larger stress to initiate deformation (i.e. it has a larger yield stress).

Fig. 3 shows the potential energy versus strain up to strain 2 for the three cooling rates and the fastest and slowest strain rates. The potential energy can be rather slow in converging to its steady state value, especially for the highest strain rate and lowest cooling rate, where it appears to converge around strain 2. This is despite that the shear stress has typically converged before strain 1. The fact that potential energy must also be monitored to ensure steady state conditions was discussed by Singh et al. [33].

V. IDENTIFYING ISOMORPHS IN NON-EQUILIBRIUM SITUATIONS

In this section we present, test and compare different methods for generating isomorphs in non-equilibrium situations, inspired by the equilibrium methods discussed in Sec. II B. Some involve fluctuations from runs at a single state point. Others involve an iterative procedure involving two state points to get certain quantities to match. Different methods disagree by increasingly large amounts as the density factor increases, but this rate of increase decreases with increasing initial density. The latter must be true since at sufficiently high densities the LJ potential is indistinguishable from the repulsive IPL 12 term; the convergence to pure IPL-12 behavior is slow, however. To compare different methods, we use as a test case glasses cooled at $10^{-5}$ (LJ units) and sheared at $10^{-3}$ (reduced units), and the case of a density increase of 10% from 1.183 to 1.301, for glasses cooled at rate $10^{-3}$; with reduced strain rate $10^{-5}$; NVT refers to NVT simulations of $10^{5}$ steps at $\rho_{i}, T_{i}$. The temperature ratio that best matches the flow stress is 1.623, listed in the last line of the table.

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Matching flow stress $SSS = 1.623$ 0.4869

TABLE I: Comparison of methods for identifying isomorphic temperature upon raising density by 10% from $\rho_{i} = 1.183$ to $\rho_{f} = 1.301$, for glasses cooled at rate $10^{-5}$ to $T_{f} = 0.3$. SSS refers to steady state shearing at $\rho_{i}, T_{i}$, data taken between strains 2 and 4, with reduced strain rate $10^{-5}$; NVT refers to NVT simulations of $10^{5}$ steps at $\rho_{i}, T_{i}$. The temperature ratio that best matches the flow stress is 1.623, listed in the last line of the table.

In the absence of true equilibrium the next best thing is steady-state deformation. Thus one could look at $U,W$ fluctuations in the steady state and identify an exponent $\gamma$. This approach was used in our previous work [20] and worked well there where the focus was on steady-state behavior and the density changes were fairly small, up to 9%. In the present work we include some glasses cooled relatively quickly; in these cases $\gamma$ determined from NVT fluctuations could be sensitive to aging effects and thus hard to define precisely. Nevertheless for comparison we have determined $\gamma$ from NVT simulations in a glass and determined the temperature ratio using the analytic formula, Eqs. 5. We show the result for a glass cooled at the fastest rate, but have checked that using the slowest cooled glasses gives a difference less than 0.1% in the resulting temperature ratio.

A. Density scaling exponent from fluctuations

One approach is to ignore the fact that the glass is out of equilibrium and determine the isomorphs in the usual way by simulating an NVT ensemble and using the $U,W$ fluctuations to determine the density scaling exponent $\gamma$. This approach was used in our previous work [20] and worked well there where the focus was on steady-state behavior and the density changes were fairly small, up to 9%. In the present work we include some glasses cooled relatively quickly; in these cases $\gamma$ determined from NVT fluctuations could be sensitive to aging effects and thus hard to define precisely. Nevertheless for comparison we have determined $\gamma$ from NVT simulations in a glass and determined the temperature ratio using the analytic formula, Eqs. 5. We show the result for a glass cooled at the fastest rate, but have checked that using the slowest cooled glasses gives a difference less than 0.1% in the resulting temperature ratio.
FIG. 4: The five methods to obtain the temperature ratio $T_f/T_i$ used to identify the state point $\rho_f, T_f$ isomorphic to state point $\rho_i, T_i$ from simulations at the latter. The example here uses reference density and temperature $\rho_i = 1.183$ and $T_i = 0.3$ and a starting configuration cooled at $R_e^\circ = 10^{-5}$. We consider a new density $\rho_f = 1.4\rho_i = 1.301$. Black indicates results from NVT simulations and red is for the steady state from a shear simulation with the highest (reduced) strain rate $\dot{\varepsilon} = 10^{-3}$. (a) Scatter-plot of the virial $W$ versus potential energy $U$. The slopes (correlation coefficient) of the two fits are 5.014 (0.869) and 5.143 (0.859) respectively, where the slopes can be considered estimates of the density scaling exponent $\gamma$, which yields the temperature factor via Eqs. (5) and (7). For (b), (c) and (d) the system was sampled at regular intervals during the simulation and configurations uniformly scaled to $\rho_f$; the potential energy, forces, and shear stress were calculated on the scaled configurations, denoted with subscript $f$. (b) Scatter-plot of $U_f$ against $U_i$ (DIC-pp). The slopes (correlation coefficient) are 1.593 (0.975) and 1.609 (0.972) respectively. Here the slopes correspond directly to the temperature ratios. (c) Scatter-plot of $\sigma_f$ against $\sigma_i$. The slopes (correlation coefficient) are 1.755 (1.00) and 1.757 (0.999). Here the temperature ratio is the slope divided by the density ratio 1.1. (d) Temperature ratio given by the force method FM (blue), Eq. (9), and modified force method (green), Eq. (10), from the same shear simulation. The dotted horizontal lines indicate the corresponding temperature ratios from the NVT simulation. Table I gives the results of the different methods.

B. Direct isomorph check based on potential energies and shear stress

Next we apply the DIC to a shearing simulation at a (reduced) strain rate $10^{-3}$, data shown in Fig. 4(b), along with corresponding NVT data. Determining the slope gives a direct estimate of the temperature factor, 1.609 from the steady-state and 1.593 in NVT. These are equal to the estimates from combining $\gamma$ and the analytical formula (consistent with $\gamma$ being the infinitesimal version of the DIC). Both these methods are based on the fluctuations of potential energy during the steady state or NVT, and how these fluctuations change as density is changed.

Fig. 4(c) shows the shear-stress based DIC. The observed slope when plotted the scaled versus unscaled shear stresses is not the temperature ratio, but includes also a factor of the density ratio $\rho_f/\rho_i = 1.1$. After dividing the latter out the temperature ratio estimate from steady state fluctuations is slightly lower (0.7%) than the corresponding energy-based DIC estimate, see Table I. Interestingly, the correlation is much higher for the stress-based DIC than for the energy-based DIC, and the difference between NVT and SSS estimates is much smaller than for the energy-based DIC, at only 0.1%. These two estimates are also very close to the NVT energy-based DIC estimate.

C. Force Method

In a recent paper Schröder has presented a method for determining the temperature ratio corresponding to a given density scaling from a single configuration, based on analyzing forces rather than energies[21]. Given as before densities $\rho_i$ and $\rho_f$, and temperature $T_i$, the estimated isomorphic $T_f$ is given using the force method by

$$T_f = T_i \left( \frac{\rho_i}{\rho_f} \right)^{1/3} \frac{|F_f|}{|F_i|} \quad (9)$$

As before, the boldface $F$ represents the forces acting on all $N$ particles. The above expression was derived by minimizing a certain mismatch function between reduced forces at the two densities, but it can be interpreted quite simply: it is the temperature for which the magnitude of the force vector is the same in reduced units for both densities. For an isolated configuration in a possibly non-equilibrium context the concept of temperature may not be entirely well defined, and in particular, $T_i$ may not necessarily be known. Dyre has shown, however, that a temperature can be defined for individual configurations, based on their potential energy, called the systemic temperature[15][36]. The force method can then also be interpreted as giving the ratio of systemic temperatures upon a change of density.

Yet another interpretation of the force method is that it is analogous to the DIC, but considering energy fluctuations associated with infinitesimal displacements of all $3N$ coordinates from a given configuration. However in that case expression (9) corresponds not to the linear regression slope of the DIC plot but to a symmetric slope equal to the ratio of standard deviations of the two variables. A version of the force method more directly analogous to the DIC would involve the asymmetric linear regression slope, giving the following "modified force method" expression for the new temperature

$$T_f = T_i \left( \frac{\rho_i}{\rho_f} \right)^{1/3} \frac{F_i \cdot F_f}{|F_i| \cdot |F_f|} \quad (10)$$

The modified force method gives a slightly lower temperature estimate. Since both force methods only re-
require a single configuration to give a temperature ratio $T_2/T_1$, they can be applied repeatedly through a simulation, giving an immediate estimate of statistical errors and possible systematic changes. Figure 4(d) shows the temperature ratios for both force methods. There is a clear systematic decrease in the estimated temperature ratio for the original force method as the strain increases from zero to steady state conditions, from 1.653 to 1.649. The former value coincides with the estimate from an NVT simulation, indicated with a short horizontal line. It is also clear that the statistical fluctuations are rather small in the steady state—the differences appear only in the fourth decimal, so that the estimate from a single configuration would indeed give a precise estimate of the ensemble average. The figure shows also the estimate from the modified force method, which is systematically lower by about 0.7%. The SSS values are lower than the NVT values for both force methods, by about opposite to what is seen in the $\gamma$ and DIC methods, and the differences are small, of order 0.25%.

D. Comparison of methods for varying density jumps

In this subsection we compare the methods described so far—the methods for generating isomorphs that involve simulations at one state point, and use data from that simulation, including calculation of quantities after applying a uniform scaling to sampled configurations. We have seen above that for the initial density 1.183 and a density increase of 10%, slightly different estimates of the temperature ratio are given by the different methods, which are summarized in Table I. The largest temperature factor is given by the force method in the steady state flow, while the smallest is given by either the $\gamma$ method or DIC using NVT data or the stress-based DIC using either NVT or SSS data. Concentrating from now on on the SSS estimates, the spread between highest and lowest is 3.5%. We next consider how this variation depends on the size of the density jump. Fig. 5(a) shows the temperature ratios from the aforementioned methods versus density. For small density changes, all these methods return similar results with little discrepancy. This discrepancy increases with larger density spans, indicating that one needs to be more cautious when finding isomorphs under such situations. We note here that the SSS data is obtained from a shear simulation at $\rho = 1.183$ and $T = 0.3$ cooled with $\dot{\epsilon} = 10^{-5}$ with $\dot{\epsilon} = 10^{-5}$. Other cooling rates and strain rates were also checked and found to return almost the same results, in particular the order of temperature-estimates is identical. On the other hand, the same calculation of temperature ratios (TR) but at a 10% higher starting density shows much less difference between various methods, as shown in Fig. 5(b). The higher the starting density is, the closer the system is to the IPL system, the more accurate the isomorph approximation is, leading to the overall smaller $TR_{\text{max}}/TR_{\text{min}}$ in Fig. 5(b).

E. Matching the flow stress

We are primarily interested in identifying isomorphs as curves along which physically relevant quantities, a key example being the flow stress, are invariant (in reduced units). Therefore the question is now which of the above methods actually yields the most invariant flow stress? Figure 6(a) shows for density 1.301 the reduced flow stress obtained by simulating at several temperatures, corresponding to some of the temperature estimates based on fluctuations. Panel (b) of the figure for NVT simulation (NVT) 10$^7$ steps and dashed lines are for steady state (SSS). Inset zooms in for the largest two densities. Bottom panel: the ratio between the highest and lowest temperature factors of the SSS from the top panel versus density. Solid line starts at $\rho = 1.183$, and dashed line starts at $\rho = 1.301$. For our lowest density the value of the correlation coefficient $R$, is around 0.86-0.87 (see the caption to Fig. 4), lower than the typical criterion of 0.9 for good isomorphs, therefore it is not surprising that the methods give diverging estimates. For the next lowest density, 1.301, the value of $R$ is 0.972, substantially higher, and therefore one can expect less divergence between the different methods, as the potential energy landscape becomes increasingly well approximated by that of an IPL.
FIG. 6: The reduced flow stress $\tilde{\sigma}_f$ and reduced peak stress $\tilde{\sigma}_p$ against temperature near the point of matching stress at $\rho_1 = 1.301$ (left two panels) and $\rho_9 = 2.789$ (right two panels). Same cooling rate and strain rate as in Fig. 1. Solid black lines are linear fits. Gray horizontal lines indicate the $\sigma_f$ in panel (a) and (b), and $\sigma_p$ in (c) and (d) at the reference density with shaded region indicating error. Arrows in panel (a) and (b) point to $T$ estimated using: (i) DIC stress method; (ii) DIC PE method; (iii) WU/analytics; (iv) FMMOD; (v) FM.

FIG. 7: The isomorph determined by matching flow stress. The large black diamond indicates the reference state point. The two black squares represent points whose temperatures were identified by matching the reduced flow stress to that of the reference, using the linear fits in Fig. 6 and the red diamonds are points whose temperatures have been determined by interpolation between the black squares, using Eq. (11).

shows a similar plot for the highest simulated density; here the trial temperatures were not those given by the other methods, but chosen to span a similar range. There is a clear negative linear dependence of the reduced flow stress on temperature, reflecting that barriers to flow can be crossed more easily at higher temperature (they require smaller external driving). The arrows indicate the temperatures determined by the various methods, which clearly do not match the reference flow stress within errors. The method that comes closest is the modified force method. However the linear fits to the temperature dependence of the flow stress can be used to accurately identify the temperature at which the $\tilde{\sigma}_f$ matches its reference value. This will be the basis for how to generate isomorphs.

Panels (c) and (d) of Fig. 6 show the measured reduced peak stresses at the same two densities and and the same temperatures as the flow stress in panels (a) and (b). Like the flow stress, the peak stress also has a negative linear correlation with temperature, although the larger errors combined with the limited temperature range in panel reduced the apparent correlation in (c). Comparison with the value at the reference density indicated by the grey bars presages one of our main results, that for high density changes no temperature can be found which matches both the flow and peak stresses with their values at the reference state point. With all this discussion of invariant, or not quite invariant, stresses we remind the reader that the real (i.e. non-reduced) shear stress involves a factor of $\rho k_B T$ which changes by over two orders of magnitude over the density range studied here.

A pragmatic approach to determining isomorphic temperatures is to take as our definition of the best empirically determined isomorph whose reduced flow stress matches that at the reference density. This is what we do from now on. The procedure of simulating several temperatures at each density in order to make a linear fit would be very time consuming if it should be done at each density of interest. To save work we can instead use the analytic expression, Eqs. (5) and (8). For studying the isomorphs we consider from now on ten different densities, labelled with subscripts starting from zero, as $\rho_0 = 1.183$, $\rho_1 = 1.1\rho_0$, ..., $\rho_9 = (1.1)^9 \rho_0$. In applying the analytic expression for isomorphs, we have to treat $\rho_0$ separately. Related to its somewhat low value of the correlation coefficient $R$ (Fig. 4) and the fact that methods for determining isomorphic temperature starting from this density diverge rather quickly (Fig. 5), it turns out that no parameterisation of the analytic formula can match the reduced flow stress over the full range from $\rho_0$ up to $\rho_9$. Such a parameterization can be found for the range $\rho_1$ to $\rho_9$, however. Thus we work as follows: Given the reduced flow stress at $\rho_0$ (and $T_0 = 0.3$) we use the linear fits in Fig. 6(a,b) to determine the temperatures of matching reduced flow stress at densities $\rho_1$ and $\rho_9$, respectively. From Eq. (8) with $\rho_2$ replaced by $\rho_0$, and using these fit-determined temperatures $T_1$ and $T_9$ we fix the parameter $B/A$. Finally for the remaining densities $\rho_2$, ..., $\rho_9$ we determine the isomorphic temperatures from Eq. (5) in the form

$$T_i = T_1 \frac{h(\rho_i)}{h(\rho_1)} = T_1 \frac{\rho_i^4 - (B/A)\rho_i^2}{\rho_1^4 - (B/A)\rho_1^2}$$

(11)

Figure 7 illustrates the construction of the isomorph.
TABLE II: The densities and temperatures along the isomorph identified through matching the flow stress at the first, second, and last densities, and then using the analytical method to obtain the temperatures in between.

<table>
<thead>
<tr>
<th>Density</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.183</td>
<td>0.3</td>
</tr>
<tr>
<td>1.301299</td>
<td>0.487031</td>
</tr>
<tr>
<td>1.431428</td>
<td>0.774540</td>
</tr>
<tr>
<td>1.574571</td>
<td>1.208396</td>
</tr>
<tr>
<td>1.732028</td>
<td>1.859225</td>
</tr>
<tr>
<td>1.905231</td>
<td>2.831010</td>
</tr>
<tr>
<td>2.095754</td>
<td>4.276669</td>
</tr>
<tr>
<td>2.305330</td>
<td>6.429943</td>
</tr>
<tr>
<td>2.535863</td>
<td>9.593855</td>
</tr>
<tr>
<td>2.789449</td>
<td>14.279829</td>
</tr>
</tbody>
</table>

The resulting densities and temperatures are listed in Table II. These values were determined by matching the flow stress using the highest strain rate (reduced value $10^{-3}$) (and fastest cooling-rate, though that should not matter for the flow stress). Rather than separately repeat this procedure for identifying isomorphic temperatures for the other strain rates we take as a working hypothesis that the isomorphs in the $\rho - T$ plane determined by matching reduced flow stress do not depend on which reduced strain rate was used. The validity of this hypothesis will be investigated in the following. The next step is the shearing deformation simulations. These are still very time-consuming, because at each density, and the corresponding temperature determined by the above procedure, 40 independent runs were carried out. This was repeated for all three cooling rates and all three strain rates. The stress-strain curves shown below are averages over the 40 runs in each case.

VI. ANALYSIS OF STRESS-STRAIN CURVES

A. Non-invariance of stress peaks

With the protocol for determining the putative isomorph established, we now present our main results. Figure 8 shows the full (reduced) stress-strain curves for all densities along the isomorph generated as described in Sec. IV E using reduced strain rate $10^{-3}$ and initial configurations cooled at rate $R_{c,0} = 10^{-5}$. The initial elastic parts of the curves overlay, showing that the elastic shear modulus is invariant in reduced units along the isomorph. In particular, a closer inspection of the data (not shown here) shows collapse within the noise for the initial 1% or so of strain. Also it is clear that the steady state flow stresses match, at least within the fluctuations—this is expected since the isomorph was constructed to have invariant flow stress. Nevertheless it serves as a check that the analytic formula for constructing the isomorph fits the data for 10% strain around the maximum stress using a fourth-degree polynomial and identify the maximum of the data for $10^{-3}$, $10^{-4}$, and $10^{-5}$ (circle, square, triangle). Each point in (a) is an average of 40 shear simulations (on 40 individual configurations, or 30 for $\dot{\epsilon} = 10^{-5}$) and the uncertainties are computed as described in Sec. III B. For the peak stress [panel (b)], we first divide the 40 shear runs into 5 groups and obtain 5 averaged stress and strain curves. We then fit the data for 10% strain around the maximum stress using a fourth-degree polynomial and identify the maximum of the fit as the $\tilde{\sigma}_p$. The error is the standard deviation of the 5 values divided by $\sqrt{5}$. The three families in (a) correspond to $\dot{\epsilon} = 10^{-3}, 10^{-4}, 10^{-5}$ from top to bottom respectively. The errors are all smaller than the marker size. The position of the gray bars in (a) are the reference $\tilde{\sigma}_f$ (at $\rho_1$ cooled with $R_{c,0} = 10^{-5}$ and sheared with $\dot{\epsilon} = 10^{-3}$) and the width of the bar indicates the reference $\tilde{\sigma}_f$ plus or minus the uncertainty.

FIG. 8: Reduced stress-strain curves along isomorph determined by the procedure illustrated in Fig. 7. Glasses at cooled (at lowest density) at rate $R_{c,0} = 10^{-5}$ and sheared at reduced strain rate $\dot{\epsilon} = 10^{-3}$.

FIG. 9: (a) $\tilde{\sigma}_f$ and (b) $\tilde{\sigma}_p$ against density along the isomorph for $R_{c,0} = 10^{-5}, 10^{-6}, 10^{-7}$ (black, red, blue), and $\dot{\epsilon} = 10^{-3}, 10^{-4}, 10^{-5}$ (circle, square, triangle). Each point in (a) is an average of 40 shear simulations (on 40 individual configurations, or 30 for $\dot{\epsilon} = 10^{-5}$) and the uncertainties are computed as described in Sec. III B. For the peak stress [panel (b)], we first divide the 40 shear runs into 5 groups and obtain 5 averaged stress and strain curves. We then fit the data for 10% strain around the maximum stress using a fourth-degree polynomial and identify the maximum of the fit as the $\tilde{\sigma}_p$. The error is the standard deviation of the 5 values divided by $\sqrt{5}$. The three families in (a) correspond to $\dot{\epsilon} = 10^{-3}, 10^{-4}, 10^{-5}$ from top to bottom respectively. The errors are all smaller than the marker size. The position of the gray bars in (a) are the reference $\tilde{\sigma}_f$ (at $\rho_1$ cooled with $R_{c,0} = 10^{-5}$ and sheared with $\dot{\epsilon} = 10^{-3}$) and the width of the bar indicates the reference $\tilde{\sigma}_f$ plus or minus the uncertainty.
is reliable. However, the peak in the stress-strain curve is clearly not invariant—it decreases systematically with increasing density, by about 20%, as the density rises to 2.8. Thus we have a clear deviation from isomorph invariance when the transient response to shearing is considered.

We find similar results for the other strain rates and cooling rates. Rather than show all of those stress-strain curves here, we instead extract the flow stress and peak stress from each stress strain curve, and plot these as a function of density in Fig. 9(a) and (b), respectively; the curves themselves can be found in Appendix A. Before considering the isomorphic behavior, we note that as expected, slower strain rates decrease both the peak stress and the flow stress; and slower cooling rates increase the peak stress but leave the flow stress unchanged. The isomorphic behavior is understood through the dependence (or non-dependence) of these quantities on density along the isomorph. In part (a) of the figure we see that the flow stresses are indeed flat within errors, as they have been constructed to be (the errors are comparable to, though smaller than, the symbol sizes). This plot also confirms our hypothesis that the isomorph determined by requiring invariant flow stress at one cooling rate and reduced strain rate is valid also for the others.

Part (b) of the figure shows the evolution of the reduced peak stress as a function of density along the isomorph. The trend is similar for all cooling and strain rates, with more or less similar relative drops of peak stress as density increases. In all cases the bulk of the drop occurs over densities ρ1 ≃ 1.3 to ρ5 ≃ 1.9, after which the change in reduced peak stress for each 10% increase in density is reduced. Interestingly the change between densities ρ0 and ρ1 is also smaller. Above density 1.9, δρ appears to continue to decrease linearly, which is surprising, since one would expect it to flatten out in the high-density limit since pure-IPL behavior begins to dominate.

To summarize the influence of density on reduced peak stress, Table III gives the magnitudes of the relative stress drops over the full density range for all strain and cooling rates. The only apparent trend here is that both faster cooling and faster shearing tend to give slightly smaller drops, around 20% instead of around 24%. An apparent outlier is the value for the highest cooling rate and the lowest strain rate (black triangles), where the change in reduced peak stress is quite limited, only 11%. This case corresponds to the least stable glass being very slowly deformed, and has the lowest peak stress to start with. To provide a different view of the influence of cooling rate and strain rate, Table IV shows the ratio between peak stress and flow stress at the lowest density. This indicates indeed that the same case of lowest strain rate and fastest cooling has the lowest ratio of peak to flow stress at the lowest density, 1.31. However there does not seem to be, upon comparing Tables III and IV a general correlation between fractional drop of peak stress with increasing density, and initial ratio of peak to flow stress. The most that can be said probably is that when the latter ratio is very low, there is less contrast between the non-flowing and flowing states, in the sense that the microscopic barriers to be crossed are not much different to start with and therefore there is less room for variation along the isomorph.

### Table III: Fractional change of $\tilde{\sigma}_p$ between the highest- and lowest-density isomorph points for different $R_{c,0}$ and $\tilde{c}$ combinations.

<table>
<thead>
<tr>
<th>$R_{c,0} = 10^{-5}$</th>
<th>$\tilde{c} = 10^{-3}$</th>
<th>$\tilde{c} = 10^{-4}$</th>
<th>$\tilde{c} = 10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.204 ± 0.011</td>
<td>0.213 ± 0.014</td>
<td>0.114 ± 0.009</td>
<td></td>
</tr>
<tr>
<td>0.211 ± 0.006</td>
<td>0.243 ± 0.008</td>
<td>0.236 ± 0.012</td>
<td></td>
</tr>
<tr>
<td>0.207 ± 0.010</td>
<td>0.242 ± 0.006</td>
<td>0.236 ± 0.008</td>
<td></td>
</tr>
</tbody>
</table>

### Table IV: Ratio of $\tilde{\sigma}_p$ to $\tilde{\sigma}_f$ for the lowest-density isomorph points for different $R_{c,0}$ and $\tilde{c}$ combinations.

<table>
<thead>
<tr>
<th>$R_{c,0} = 10^{-5}$</th>
<th>$\tilde{c} = 10^{-3}$</th>
<th>$\tilde{c} = 10^{-4}$</th>
<th>$\tilde{c} = 10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.87</td>
<td>1.67</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>2.16</td>
<td>1.99</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>2.43</td>
<td>2.37</td>
<td>2.04</td>
<td></td>
</tr>
</tbody>
</table>

### B. Equivalent configurations in stress peak?

![FIG. 10: Comparison between stress-strain curves obtained from shearing at the lowest density (blue), computing the stress from the same configurations scaled to the highest density (green), and actually shearing at the highest density (orange) with $\tilde{c} = 10^{-3}$ and $R_{c,0} = 10^{-7}$.](image)
stress-strain curve based on scaling configurations statically. This is similar to what is done in the stress-DIC method proposed above, but rather than use it to generate an isomorph we use it to compare the potential energy surface sampled by the same reduced configurations at different densities. If the “fake” high-density stress-strain curve matches that actually simulated at high density then the conclusion would be that configurations at high stress are essentially equivalent to the corresponding ones at low densities but that the interactions are softened more at high densities and high stress than for high densities at lower stress (i.e. the steady state). If they do not match then something different must be happening in the microscopic dynamics during the stress peak. Fig. 10 shows the result of this check. The curve generated from configurations sampled at the reference density $\rho_0$ and scaled $\rho_9$ (green) matches the curve at the reference density well, except for a small difference in normalization, and does not match the curve obtained from simulating at the high density $\rho_9$, which has the lower stress peak. This shows that the second possibility mentioned above must be the case: the particles undergo non-equivalent motion when simulated at the higher density. We examine what this non-equivalence is in the next sub-section.

VII. MICROSCOPIC BEHAVIOR

The results of the previous section concern macroscopic mechanical properties. In this section we study variation of microscopic structure and dynamics, both at the particle level and at slightly larger length scales where we study inhomogeneities in the strain profile. The results of these different analyses suggest an explanation for the failure of the stress peak to collapse.

A. Invariance of pair structure and single-particle dynamics in the steady state

In this subsection we consider particle-level measures of structure and dynamics properties, in particular self-diffusion and pair-structure. To investigate self-diffusion we plot in Fig. 11(a) the mean squared transverse displacement (MSD) in reduced units, as a function of reduced time, for all densities along the isomorph at reduced shear rate $\dot{\epsilon} = 10^{-4}$. By transverse we mean that only components of displacement orthogonal to the shearing direction are included. The quality of the collapse is extremely good, so that it is not obvious to the eye that there are in fact ten curves plotted. This plot is based on data from a single run for each density, since there is sufficient averaging over particles to get good statistics for single-particle dynamics.

Fig. 11(b) shows the radial distribution function (RDF) for AA pairs along the same isomorph. The collapse here is also very good, similar to what is seen in equilibrium liquids[11]. Both the MSD and RDF are determined from configurations drawn from the steady state. The quality of the invariance apparent in Fig. 11 confirms that the isomorph has been determined correctly. The non-invariance evidenced by the failure of the peak stress to collapse seems therefore to be restricted to the transition from non-flowing to flowing states. This will be discussed more below.

B. Variation in spatial homogeneity

We now present results of analyzing strain profiles and local measures of plastic activity in order to determine whether the variation of peak stress can be associated with some systematic difference in the spatial organization of the initiation of flow, for example if flow is more or less localized in the peak at higher densities compared to lower densities.

The first indicator we consider is the non-affine displacement at the particle level. Recall that shearing mo-
tion occurs in the $x$-direction, while the gradient is in the $y$-direction. We first define the affine displacement $\Delta \vec{r}_{A,i}$ for particle $i$ as $\Delta \vec{r}_{A,i} = \Delta \vec{r}_{i} - \vec{r}_{i}$, where $\vec{r}_{i}$ is the position of particle $i$ in the gradient direction and $\vec{r}$ is the velocity direction. This is simply the displacement associated with the macroscopic strain imposed on the system, which is known. Under shear, local rearrangements cause deviations from this affine motion. We define such deviation as the non-affine motion $\Delta \vec{r}_{NA,i} = \Delta \vec{r}_{real,i} - \Delta \vec{r}_{A,i}$, where $\Delta \vec{r}_{real,i}$ is the full displacement of particle $i$. We expect that each component of the non-affine displacement is symmetrically distributed about zero, but it is possible that the distributions for the different components could be different. Figure 12 shows the variance of the non-affine displacement for each component, in reduced units. The data in part (a) of the figure are for displacements between undeformed configurations (strain 0) and corresponding configurations deformed to strain 0.12. The figure thus contains information about particle motions during the transition from the non-flowing to the flowing state, specifically those associated with the stress peak. As a function of increasing density the variance for each component increases systematically, indicating a non-isomorph invariant behavior. In part (b) of the figure, data for a similar strain interval, but taken from the steady regime is shown. Here no systematic variation as a function of density is apparent. Systematic differences between components are visible, with the variance for the $x$-component of non-affine displacement being highest both in the transient case and in the steady state. Chen et al. studied distributions of non-affine motion in experiments on colloids; their Fig. 8 shows PDFs of non-affine motion in the three different directions. The distribution for the out-of-plane direction (their $y$-direction, corresponding to our $z$-direction) is slightly narrower than for the other two directions, which is consistent with what we see.

Another, related measure of spatial inhomogeneity is to consider the displacement profiles obtained by binning particles according to their $y$-coordinate and averaging the $x$-displacement for all particles in a bin. This gives a probe of systematic variation in the gradient direction, while averaging over other directions. An example is shown in Fig. 12 for a 12% strain interval from the steady state in a particular run. A clear systematic deviation from the affine profile is visible: the system exhibits two distinct regions with the strain differing by a factor of two as indicated by the linear fits (note that the region of the left is connected to that on the right via the periodic boundary conditions). This coexistence of regions with differing strain (rates) is termed shear-banding. Profiles for different runs exhibit somewhat similar shapes, with mostly a single region of higher strain, more or less sharply delimited from the rest of the system, with varying contrast (i.e., difference in strain). To quantify this contrast and look for systematic variations along the isomorph we take the mean squared deviation of each point from the affine line, yielding a norm of the (non-affine) displacement profile. For the example in Fig. 13 the norm is 0.022. Note this measure of non-affine motion differs from that presented in Fig. 12 in the initial averaging within a $y$-bin before squaring and further averaging over bins. We calculate the mean norm from the 40 runs at each density, and plot these as a function of density in Fig. 14. As with Fig. 12 we see a clear trend in the transient data, and no discernible trend in the steady state data. This suggests that at lower density there is a greater tendency for quasi-shear-banding to occur during the stress peak. This decreases with increasing density, particularly over the first three densities. The steady-state values in panel (b) are mostly below the low-density transient values; there are a couple of exceptions to this but no overall trend. We have only looked at a specific interval covering 12% of strain in all cases; an interesting question for future work is to what extent a given quasi-shear-band persists over longer amounts of strain. Interestingly, and apparently counterintuitively, the trend visible for the red data points in Fig. 14 is in the opposite direction to those shown in Fig. 12 (a). An interpretation which encompasses both behaviors would be that the stress peak at the lower densities coincides with particles exhibiting less overall non-affine motion than at higher densities, but where whatever non-affine motion is actually present is more coherent, and gives a larger signal in the displacement profiles.
give varying results for the temperature at which the new state point should be isomorphic to the starting, or reference state point. The difference is up to 20% for density changes of a factor up to about 2.3 (compared to an overall temperature variation up to a factor of 50). For moderate density changes one can at least argue that any of these methods give at least a reasonable estimate of isomorph temperatures; in particular the force method or its modification can do so with little computational cost. However one cannot be sure about the quality of the isomorph determined this way. The dream of being able to make directly reliable isomorph jumps in non-equilibrium situations is thus not yet realized. Presumably one could still make small jumps of 1-2% in density, simulating at each step and using a fluctuation method to compute the next temperature, as in the original isomorph paper[1]. This would be time consuming, but perhaps would not require as many independent runs as we have used here.

Given these difficulties our strategy has been to require the reduced flow stresses to match at all densities as a practical method of identifying the isomorph. Because of intrinsic fluctuations in the shear stress during steady state deformation[20], an accurate determination of the flow stress requires a combination of long runs and/or many independent runs, and is therefore computationally demanding, especially at the slowest strain rates. But it was sufficient for our purposes in this paper. The quality of this choice of determining isomorphic temperatures for given density jumps is evidenced by the invariance of microscopic dynamics and structure, Fig. [11].

Among the methods for identifying isomorphs that we have tried, the most traditional are the WU/analytic method and the DIC, which are consistent with each other, and yield flow stress at the estimated temperature which is larger than the reference flow stress (in reduced units). Equivalently they underestimate the temperature needed to collapse flow stress, see Fig. [6]. The force method[21] and its modification FM-mod are more recent; these yield smaller reduced flow stresses than the reference; equivalently they overestimate the temperature to match the flow stress. The DIC and the WU/analytic method are based on matching short time potential energy fluctuations; such fluctuations are dominated by vibrational motions. The force-based methods can be considered as referring also to energy differences—the differences associated with infinitesimal displacements of particles. But these scale somehow differently with changes of density than ordinary energy fluctuations, giving the larger isomorph temperatures. These methods sample different aspects of the potential energy surface and how it is affected by density changes, although it is not clear what the difference is exactly. The flow stress is determined by yet a third aspect of the potential energy surface, namely the barriers associated with flow. It is certainly conceivable that these are a distinct part of the potential energy surface, scaling differently than the part governing vibrational motion[14]. Why the isomorph temperature which matches the flow

VIII. DISCUSSION

The first part of this work was concerned with studying different methods for determining isomorphs in out-of-equilibrium situations. Particularly when large density changes are involved, different methods based on fluctuations (of the potential energies of a set of configurations, or of particle forces within a single configuration)
stress falls between that for the energy fluctuations and that for forces remains unclear, however. Some insight could perhaps be gained by investigating the barriers to flow explicitly using barrier finding techniques on small systems to trace the way a typical energy barrier scale differently with density. The second main result of this work is the failure of the (reduced) peak stress under shear deformation to collapse along the isomorph determined by forcing collapse of the flow stress. Simply put, no temperature can match both peak and flow stress, meaning that the relevant energy barriers scale differently with density. The analysis of section [VI B] shows that this is not simply a question of the same trajectories (in reduced coordinates) experiencing different potential energies, forces and stresses, but rather the trajectories are non-equivalent in the region of the stress peak, as evidenced by the analysis of non-affine motion. For different (reduced-unit) trajectories to result, the (reduced-unit) forces have to be different, of course. But subtle differences in the forces can lead to macroscopic differences in the trajectories, in particular the degree of shear-banding, which then leads to pronounced differences in the observed stresses. A possible explanation for a variation in the tendency for shear-banding could be that it depends sensitively on the steepness (effective IPL exponent of the potential, something that has apparently not been tested before in the literature. This could be tested by running IPL simulations with different exponents and studying the tendency to create shear bands.

The range of effective IPL exponents is quite limited for Lennard-Jones systems, varying from around 18 at low pressures to approaching 12 at the highest pressures. Potentials which exhibit more dramatic variation of effective exponent (equivalently $\gamma$) include the exponential pair potential [45] and the many-body effective medium theory potential for metallic systems [44]. Studying these systems would give additional insight, by potentially exhibiting an even more pronounced variation in the peak stress along isomorphs; it might for example by noticeable at relatively small density changes.

Finally, we note that since Fig 14 indicates that shear banding occurs also in the steady state, a varying tendency towards shear banding depending on density (via the effective IPL exponent) could actually be present in the steady state. Since we have chosen the isomorph temperatures to match the reduced steady-state shear stress we do not see this in our data (essentially because temperatures have been adjusted to compensate for it), but it could potentially underlying the failure of the fluctuation methods to predict the steady-state stress. Comparing different IPL systems under steady state shear could also shed light on this.

FIG. 15: Stress and strain curves of glasses cooled at three rates and sheared at reduced strain rate $\dot{\epsilon} = 10^{-3}$. We only show strain up to 1 so that the peak is more visible; only 4 densities are shown for clarity. The black horizontal dashed lines indicate the flow stress. These curves are where the data of Fig. 9 are derived from.

FIG. 16: Same as in Fig. 15 but now for glasses cooled at three rates and sheared at reduced strain rate $\dot{\epsilon} = 10^{-4}$.

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FIG. 17: Same as in Fig. 15 but now for glasses cooled at three rates and sheared at reduced strain rate $\dot{\epsilon} = 10^{-5}$. 

$\gamma = 10^5$ $\gamma = 10^4$ $\gamma = 10^3$
Appendix A: Stress strain curve collapse for other cooling and (reduced) strain rates

We present here for completeness the full set of strain curves for all cooling and strain rates. Figs. 15 and 17 show data for reduced strain rates $10^{-3}$, $10^{-4}$ and $10^{-5}$, respectively. The individual panels show data for the different cooling rates. By comparing panels within one figure one can see the effect of the changing cooling rate on the initial peak, while the effect of different strain rates can be seen in the flow stress–constant within each figure—varying from one figure to another. In all cases the behavior discussed in the main text, namely the decrease of reduced peak stress as a function of density along an isomorph, is clearly visible.