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## Supplement Material for "Parameter-free predictions of the viscoelastic response of glassy polymers from nonaffine lattice dynamics"

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## I. SIMULATION OF MECHANICAL SPECTROSCOPY

In order to obtain G', G'' from molecular dynamics simulations, we apply a sinusoidal shear strain to the simulation cell and measure the resulting instantaneous stress  $P_{xy}$  obtained from the virial tensor. In Fig. 1 we show an example of the data for the time dependence of  $P_{xy}$  as well as the corresponding stress-strain curves (Lissajous figures) for three frequencies at T = 0.05. The LAMMPS code was used for all shear simulations.

## II. EQUIVALENCE OF RESULTS OBTAINED FROM SIMPLE AND PURE SHEAR IN THE LIMIT OF SMALL DEFORMATIONS

In simulations we use simple shear to obtain the viscoelastic moduli. The theory, however, predicts the values of these quantities for a pure shear deformation. Here we show that in the case of small deformations the results produced by a simple shear are equivalent to the results produced by a pure shear.

The following deformation tensors for the coordinate transform  $\mathbf{r}' = \hat{u}\mathbf{r}$  for pure and simple shear, correspondingly, read:

$$\hat{u}_{\text{pure}} = \begin{pmatrix} \cos(\gamma/2) & \sin(\gamma/2) & 0\\ \sin(\gamma/2) & \cos(\gamma/2) & 0\\ 0 & 0 & 1 \end{pmatrix}, \quad (1)$$

$$\hat{u}_{\text{simple}} = \begin{pmatrix} 1 & \tan(\gamma) & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix}.$$
 (2)

We now consider only central forces with  $U(\gamma) = \frac{\kappa}{2} \sum_{ij} (r_{ij}(\gamma) - r_0)^2$ . For the pure shear:

$$\begin{aligned} r'_{ij} &= \sqrt{r^2_{ij} + 2r^x_{ij}r^y_{ij}\sin\gamma}, \left. \frac{\partial r'_{ij}}{\partial\gamma} \right|_{\gamma=0} = r_{ij}\hat{n}^x_{ij}\hat{n}^y_{ij}, \\ \frac{\partial r'_{ij}}{\partial\mathbf{r}_i} \right|_{\gamma=0} &= -\hat{n}_{ij}. \end{aligned}$$
(3)

Hence, the affine shear modulus and affine force field are (cf. definitions in the SI of [1]):

$$G_{pure}^{A} = \kappa \sum_{ij} r_{ij}^{2} \left( \hat{n}_{ij}^{x} \hat{n}_{ij}^{y} \right)^{2}, \, \boldsymbol{\Xi}_{i,\text{pure}} = -\kappa \sum_{ij}^{Z} r_{ij} \hat{n}_{ij}^{x} \hat{n}_{ij}^{y} \hat{n}_{ij}.$$
(4)

For simple shear

$$\begin{aligned} r'_{ij} &= \sqrt{r_{ij}^2 + 2r_{ij}^x r_{ij}^y \tan \gamma + (r_{ij}^y \tan \gamma)^2}, \\ \frac{\partial r'_{ij}}{\partial \gamma} \Big|_{\gamma=0} &= r_{ij} \hat{n}_{ij}^x \hat{n}_{ij}^y, \\ \frac{\partial r'_{ij}}{\partial \mathbf{r}_i} \Big|_{\gamma=0} &= -\hat{n}_{ij}. \end{aligned}$$
(5)

Since the derivatives of  $r'_{ij}$  are the same as for pure shear, the values of the shear modulus and the affine force field should be the same as well. The reason for this equivalence is that, for small deformations, pure and simple shear can be inter-converted by a solid rotation of an angle  $\gamma/2$ .

## III. CHANGE OF THE NUMBER OF NEAREST NEIGHBORS WITH TEMPERATURE

In this section, we show an insight into the dynamical changes of the bead positions in order to illustrate the reasons for the applicability of the theory at non-zero temperatures. Two beads are considered to be neighbors if the distance between their positions is smaller than 1.2. Positions of the beads are compared at every tenth of an external force period. To enumerate the number of changes, we count all new pairs which were formed, and all cases when two beads became separated, within this time. In Fig. 3 the average of change of the number of nearest neighbors is shown for three different frequencies and different temperatures. At all temperatures the beads move more in the case of low frequencies, i.e. at low frequencies the beads have time to adjust their positions and move between the cages. With an increase of temperature more and more beads become mobile, which should lead to the violation of harmonic approximation and, hence, our non-affine approach. This explains why the combination of INM and non-affine theory performs rather poorly at low frequencies. On the



Figure 1: Top: Instantaneous shear stress as a function of time for low, middle and high frequencies, correspondingly (left to right). Bottom: Evolution of the instantaneous shear stress during cycles of applied shear strain for low, middle and high frequencies, correspondingly(left to right).



Figure 2: Simple vs. pure shear deformations. (a) illustrates pure shear. The perimeter of the box is kept constant while the cross section area decreases with an increase of  $\gamma$ . (b) shows simple shear. The cross-section area stays constant while right and left side of cross section parallelogram becomes longer.

contrary, at high frequencies the bead positions are considerably more stable. Hence for high frequencies the harmonic approximation holds, which explains why nonaffine theory produces correct predictions of viscoelastic moduli values even at temperatures around and above glass transition.

A substantial difference between the low and the high frequencies comes from the time resolution, which is period dependent. In Fig. 4 we show the comparison of nearest neighbor number changes with and without shear. It is clear that shear-induced changes are largest at low frequencies.

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Figure 3: Change of the number of nearest neighbors per atom as a function of temperature and frequency of the shearing force for periods t = 0.01 (black squares), t = 0.2 (blue squares), t = 80 (red circles). The positions of atoms are compared with the time resolution of t/10. The values obtained over 10 periods were averaged.



Figure 4: The change of the neighbors in the case of sheared and undeformed samples at low and high frequencies. The absolute value of the difference is larger for the low frequency, which illustrates that at low frequencies many more atoms have time to relax their positions.