Breakdown of nonlinear elasticity in stress-controlled thermal amorphous solids

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In recent work it was clarified that amorphous solids under strain control do not possess nonlinear elastic theory in the sense that the shear modulus exists but nonlinear moduli exhibit sample-to-sample fluctuations that grow without bound with the system size. More relevant, however, for experiments are the conditions of stress control. In the present Rapid Communication we show that also under stress control the shear modulus exists, but higher-order moduli show unbounded sample-to-sample fluctuation. The unavoidable consequence is that the characterization of stress-strain curves in experiments should be done with a stress-dependent shear modulus rather than with nonlinear expansions.

Amorphous solids are created as a result of the glass transition, by cooling sufficiently rapidly certain pure liquids or mixtures of liquids so as to avoid the equilibrium phase transition to a crystalline solid. In recent years the theoretical understanding of amorphous solids has been advancing, showing that they have rather peculiar mechanical properties. In particular, it was clarified recently that generically amorphous solids do not have a regular nonlinear elasticity theory [1–3]; describing the stress-strain relation as a power series in the strain, for example, is untenable. This was shown first for athermal amorphous solids independently of the deformation protocol and later for thermal amorphous solids under strain-controlled conditions. For a wide range of (low) temperatures it is impossible to define nonlinear elastic coefficients, as they do not converge to a specific value with the increase of the system size [3]. The physical reason for this lack of convergence is the anomalous statistics of stress fluctuations in amorphous solids. It was also shown that in strain control conditions, nonlinear expansion of stress in powers of strain are not necessary, since the stress-strain curves can be fully characterized using a theoretically meaningful (local) γ-dependent shear modulus $\mu(\gamma)$ [2].

Additional interest in this phenomenon has emerged due to its relation to the putative Gardner transition [4], which is believed to exist in generic glass formers [5–7]. One of the main consequences of the Gardner transition, if it exists, is precisely the breakdown of nonlinear elasticity in the sense discussed above [8]. This increases the motivation to identify the breakdown of nonlinear elasticity in experimental system. Experiments, however, are rarely done in strain-controlled conditions since it is much easier to control the stress on a piece of material than its strain. It is therefore necessary to examine the elasticity theory of amorphous solids in stress-controlled conditions. In this Rapid Communication we examine the nonlinear elasticity theory of stress-controlled simulations, where the strain is the fluctuating quantity. The central conclusion is that also in stress-controlled conditions the nonlinear elasticity theory breaks down and should not be used in the context of amorphous solids. Using a stress-controlled simulation takes us one step closer to systems used in experiments and perhaps similar results can be obtained in future experimental measurements.

Consider the standard nonlinear elasticity theory for a solid under simple shear strain, with $\gamma = \gamma_{xy}$ being the only nonzero

component of the strain tensor. The stress is computed as a Taylor expansion around zero strain [9],

$$\sigma(\gamma) = B_1\gamma + \frac{1}{2!}B_2\gamma^2 + \frac{1}{3!}B_3\gamma^3 + \cdots, \quad (1)$$

where $\sigma = \sigma_{xy}$ is the only nonzero component of the stress tensor and

$$B_n \equiv \left.\frac{d^n\sigma}{d\gamma^n}\right|_{\gamma=0}. \quad (2)$$

Here B_1 is the usual shear modulus that is usually denoted by μ, $\mu \equiv B_1$. Inverting the power series (1) will give an equivalent expression, in terms of the derivatives $s_n \equiv \partial^n\gamma/\partial\sigma^n$:

$$\gamma(\sigma) = \gamma_0 + s_1\sigma + \frac{1}{2!}s_2\sigma^2 + \frac{1}{3!}s_3\sigma^3 + \cdots$$
$$= \gamma_0 + \left.\frac{\partial\gamma(\sigma)}{\partial\sigma}\right|_{\sigma=0}\sigma + \frac{1}{2!}\left.\frac{\partial^2\gamma(\sigma)}{\partial\sigma^2}\right|_{\sigma=0}\sigma^2 + \cdots. \quad (3)$$

The relations between the coefficients in Eqs. (1) and (3) are given by [10]

$$B_1 = \frac{1}{s_1},$$
$$B_2 = -\frac{s_2}{s_1^3},$$
$$B_3 = \frac{3s_2^2 - s_1s_3}{s_1^5},$$
$$B_4 = \frac{10s_1s_2s_3 - s_1^2s_4 - 15s_2^3}{s_1^7},$$

etc.

To compute the derivatives appearing in Eq. (3) in terms of strain fluctuations we need a statistical-mechanical expression for the mean strain. Consider a system with N particles in positions $\boldsymbol{R} \equiv \{\boldsymbol{r}_i\}_{i=1}^N$ in a volume V. When the external stress σ^{ext} is fixed, the ensemble average is provided by (see, e.g., [11])

$$\gamma(\sigma^{\text{ext}}) = \frac{\int \gamma e^{[-U(\gamma,\mathbf{R})+V\sigma^{\text{ext}}\gamma]/T}d\gamma\,d\mathbf{R}}{\int e^{[-U(\gamma,\mathbf{R})+V\sigma^{\text{ext}}\gamma]/T}d\gamma\,d\mathbf{R}}, \quad (4)$$

where T is the temperature in units where the Boltzmann constant is unity and $U(\gamma, \mathbf{R})$ is the energy of the system. One should note that Eq. (4) does not imply that the system is ergodic at temperature T; it can be trapped in a patch of phase space and is equilibrated only within that patch.

The computation of the derivatives in Eq. (3) is now straightforward [12], yielding

$$s_1 = \frac{V}{T}\left(\langle\gamma^2\rangle_0 - \langle\gamma\rangle_0^2\right),$$

$$s_2 = \left(\frac{V}{T}\right)^2\left(\langle\gamma^3\rangle_0 - 3\langle\gamma\rangle_0\langle\gamma^2\rangle_0 + 2\langle\gamma\rangle_0^3\right),$$

$$s_3 = \left(\frac{V}{T}\right)^3\left(\langle\gamma^4\rangle_0 - 4\langle\gamma^3\rangle_0\langle\gamma\rangle_0 - 3\langle\gamma^2\rangle_0^2\right.$$
$$\left. + 12\langle\gamma^2\rangle_0\langle\gamma\rangle_0^2 - 6\langle\gamma\rangle_0^4\right),$$
$$\vdots \qquad (5)$$

where the moments of the strain distribution at zero external shear stress are defined by

$$\langle\gamma^n\rangle_0 = \frac{\int \gamma^n e^{-U(\gamma,\mathbf{R})/T} d\gamma\, d\mathbf{R}}{\int e^{-U(\gamma,\mathbf{R})/T} d\gamma\, d\mathbf{R}}. \qquad (6)$$

The main question now is what statistics of strain fluctuation determine these moments. In an amorphous solid the system is confined to a compact set in a *restricted* domain of the configuration space; accordingly, for each realization of the amorphous solid the integral (6) is computed over this set of configurations that are visited by the glass particles, confined around a given amorphous structure [2,13]. This fact is the origin of sample-to-sample fluctuations; these fluctuations may either decrease or increase with the system size, depending on the moment involved. This is precisely what we need to learn using the numerical simulations described next.

Having the expressions (5) for the coefficients s_n, we will measure them below in numerical simulations for different realizations of the same glass. We will then use Eq. (4) to determine the moduli B_n. Needless to say, for each realization of the glass with N particles we will find a number for B_n. As explained, the interesting question is the sample-to-sample fluctuation, whether they decrease or increase with the system size. In other words, we will measure the distributions of these objects and the moments of sample-to-sample variances

$$\overline{(\delta B_n)^2} \equiv \overline{(B_n - \overline{B_n})^2}, \qquad (7)$$

where $\overline{(\bullet)}$ denotes the average over different realizations.

To simulate a system in which the strain is free to fluctuate we employ the variable shape Monte Carlo technique (see Refs. [14,15]), explained in more details in Ref. [11]. This method starts by defining a square box of unit area where the particles are at positions $\hat{\boldsymbol{r}}_i$. Next one defines a linear transformation $\boldsymbol{h}$, taking the particles to positions $\boldsymbol{r}_i$ via $\boldsymbol{r}_i = \boldsymbol{h} \cdot \hat{\boldsymbol{r}}_i$. The actual area of the system becomes the determinant $V = |\mathbf{h}|$. The Monte Carlo procedure employs two kinds of moves. First one performs n standard Monte Carlo moves

$$\hat{\boldsymbol{r}}_i^{\text{new}} = \hat{\boldsymbol{r}}_i^{\text{old}} + \delta\hat{\boldsymbol{r}}, \quad 1 \leqslant i \leqslant N. \qquad (8)$$

In this equation the α component of the displacement vector of a particle is given by

$$\delta\hat{r}^\alpha = \Delta\hat{r}_{\max}(2\xi^\alpha - 1), \qquad (9)$$

where $\Delta\hat{r}_{\max}$ is the maximum displacement and ξ^α is an independent random number uniformly distributed between 0 and 1. After these standard moves the transformation $\mathbf{h}$ changes according to $\boldsymbol{h}^{\text{new}} = \boldsymbol{h}^{\text{old}} + \delta\boldsymbol{h}$, where elements of the random symmetric matrix $\delta\boldsymbol{h}$ are defined by

$$\delta h_{ij} = \Delta h_{\max}(2\xi_{ij} - 1), \quad i \leqslant j. \qquad (10)$$

Here $\Delta h_{\max}$ is the maximum allowed change of a matrix element and ξ_{ij} is an independent random number uniformly distributed between 0 and 1.

In this particular case the **h** matrix was chosen to induce simple shear conditions

$$\mathbf{h} = L\begin{pmatrix} 1 & \gamma \\ 0 & 1 \end{pmatrix} = L\begin{pmatrix} 1 & \delta h \\ 0 & 1 \end{pmatrix}, \qquad (11)$$

where L is the length of the square simulation box and γ is the simple shear strain, with the volume of the system $V = L^2$ being conserved. The value of $\Delta h_{\max}$ and the maximum displacement of particle positions $\Delta\hat{r}_{\max}$ are selected to obtain a desired acceptance rate of 30%. For each kind of move the trial configuration is accepted with probability

$$P_{\text{tr}} = \min\left[1, \exp\left(-\frac{\Delta G}{T}\right)\right]. \qquad (12)$$

Here ΔG is the enthalpy change due to the move. Since in this case we chose volume-conserving transformations without any external stress applied, the expression is simply

$$\Delta G = U\left(\boldsymbol{\gamma} + \delta\boldsymbol{\gamma}, \boldsymbol{r}_i^{\text{new}}\right) - U\left(\boldsymbol{\gamma}, \boldsymbol{r}_i^{\text{old}}\right), \qquad (13)$$

where γ is the system's strain. In the current study no external stress is implemented and thus the energy difference is only due to the affine deformation itself. Thus the strain γ is free to fluctuate around some mean value. The reader should note that for any given realization of the glass the mean value of γ is not necessarily zero. Only when these means are averaged over many glassy realizations in the sense of the overline average in Eq. (7) the result should vanish.

To collect data we used the same glass former used in Ref. [3], i.e., a two-dimensional Kob-Andersen 65:35 binary Lennard-Jones mixture [16,17], slowly quenched from a liquid at $T = 0.4$ down to $T = 10^{-6}$ using molecular dynamics with the quench rate $\dot{T} = 10^{-6}$. Here temperature and all other quantities are measured in dimensionless units. The number density is $\rho = 1.162$. Each sample was than relaxed in the target temperature for $i = 5 \times 10^5$ Monte Carlo (MC) steps, in which the parameters $\Delta h_{\max}$ and $\Delta\hat{r}_{\max}$ were calibrated. Then each realization was ran with zero external stress $\sigma^{\text{ext}} = 0$ for $\tau = 5 \times 10^6$ MC steps, from which the moments of the strain fluctuations $\langle\gamma^n\rangle$ were calculated. The number of steps τ was chosen to be sufficiently large to reach saturation of the measured quantities and to be independent of the averaging window. To calculate the variances across the ensembles, for each system size $N = \{200, 500, 1000, 2000\}$ between 300 and 800 different realizations were prepared and allowed to fluctuate independently. In order to keep the data clean,
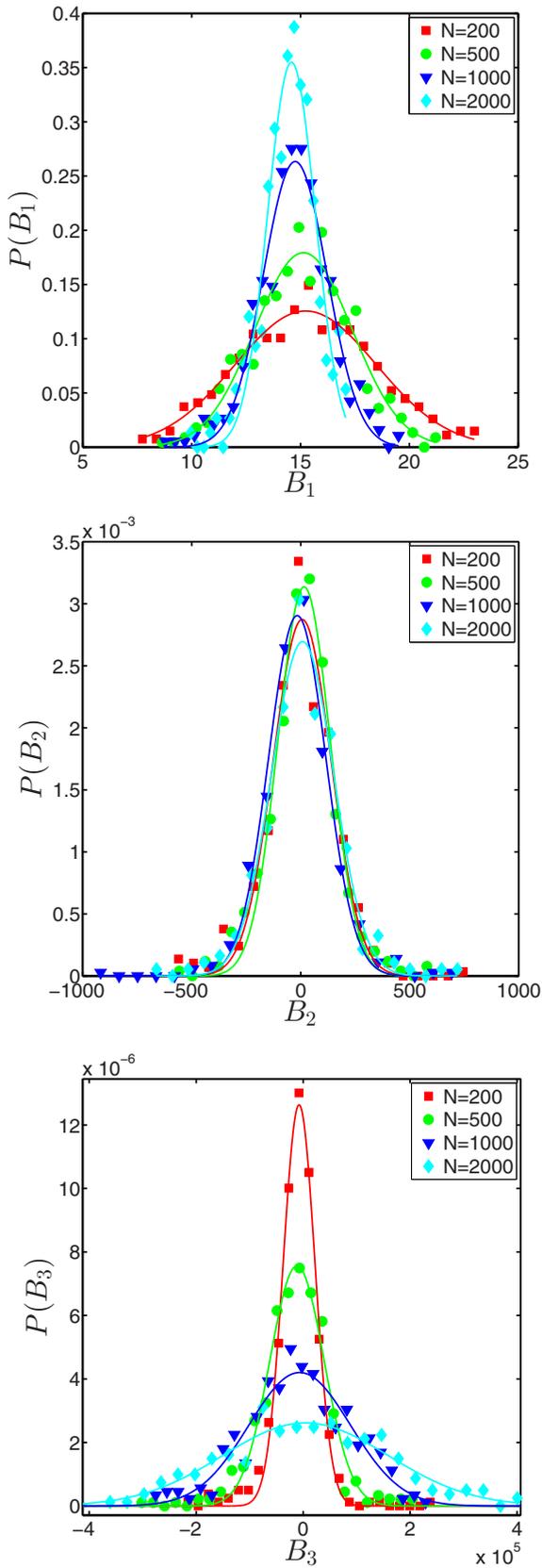
FIG. 1. Distribution of values of the first three coefficients in the expansion (1) over the realizations for different systems size. The temperature here is $T = 0.05$.
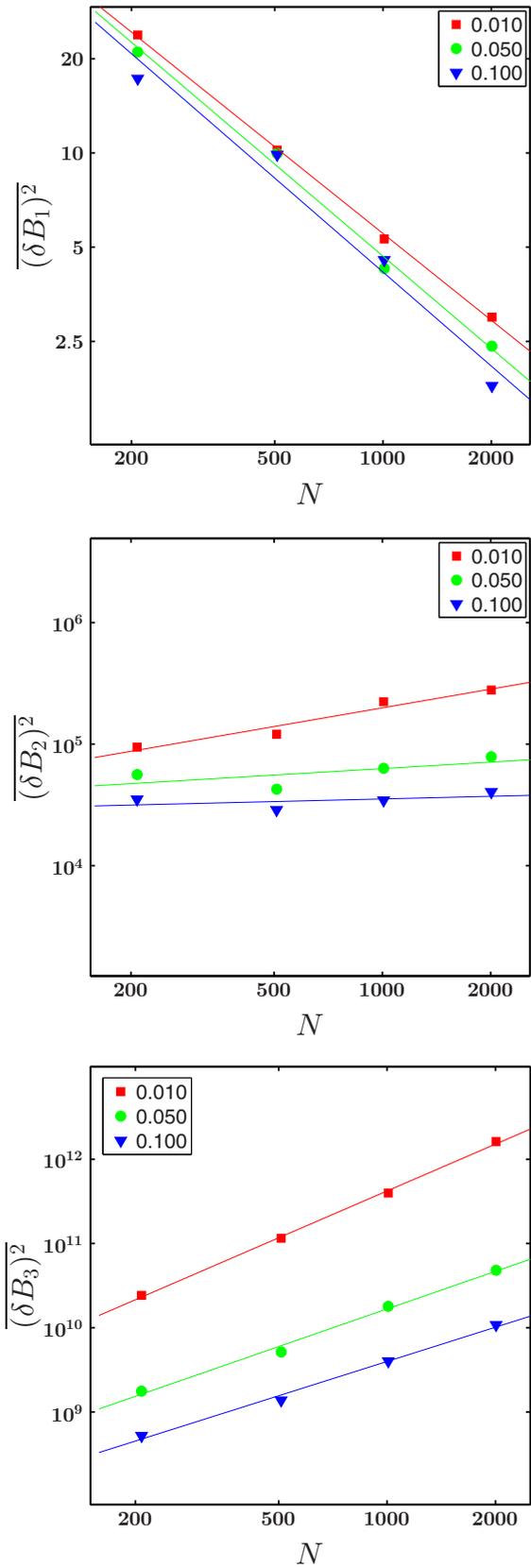
FIG. 2. System size dependence of the variances of the first three coefficients in the expansion (1). Here the temperatures are $T = 0.01$, 0.05, and 0.1.

realizations that were detected exhibiting fluctuations of the strain around two (or more) mean values were eliminated from the ensemble and were not considered for the calculation of the sample-to-sample variances.

In Fig. 1 we show the distributions of B_1, B_2, and B_3 over the different sets of realizations as explained above. The data presented here are for $T = 0.050$; similar plots were made for $T = 0.010, 0.100$. For each of the coefficients and for each system size, the values of B_n across the whole ensemble ($N = 300$–800 realizations) were binned and normalized to produce the probability density function. As in previous work (see, e.g., [1,3]), one can see that the distribution of the shear modulus $\mu = B_1$ converges to a δ function at a temperature-dependent sharp value $B_1 = 15.9, 14.9, 14.1$ at temperatures $T = 0.01, 0.05, 0.1$, respectively. The second modulus B_2 does not converge with the system size and the variance of the third modulus B_3 diverges with the system size. It is therefore interesting to examine the variances of the distribution as a function of system size, as shown in Fig. 2. The values of ensemble variance $\overline{(\delta B_k)^2}$ are presented in a log-log plot for different system sizes and are fitted to linear curves. From the data we can extract the following scaling laws:

$$\overline{(\delta B_1)^2} \sim N^{\alpha_1}, \quad \overline{(\delta B_2)^2} \sim N^{\alpha_2}, \quad \overline{(\delta B_3)^2} \sim N^{\alpha_3}. \quad (14)$$

To determine the exponents we estimate the variance by fitting a Gaussian function to the distribution. In our experience this method is superior to measuring the variance from the raw data that may have outliers that reduce the accuracy of the estimate. We measure $\alpha_1 = -0.95 \pm 0.04$ with only a slight temperature dependence. For α_3 we measure the values $\alpha_3 = 1.6 \pm 0.24$. The distribution of B_2 seems marginal and indeed the measured value of the exponent α_2 is close to zero, except at the lowest temperature, where there is an apparent weak divergence. This is in line with the results in the athermal case [1], but differs from the thermal strain-controlled ensemble [3], where a divergence was found also for the value of B_2 variance.

It is interesting to relate these findings to a recent theoretical work [8] predicting a so-called Gardner transition [4] in thermal glass-forming liquids [7,8]. The phenomenon seen in this transition is that at some temperature, lower than the glass transition temperature, there appears a qualitative change in the free-energy landscape, generating a rough surface with arbitrarily small barriers between local minima. The connection to the present work is that this is accompanied by a breakdown of nonlinear elasticity in much the same way reported here. The available theory pertains to a mean-field treatment and a comparison of exponents is probably not warranted. Nevertheless, it is interesting that the shear modulus is expected to exist and the variances of B_k with $k \geqslant 3$ are expected to diverge with the system size, in agreement with the predictions of Ref. [1] and the findings of the present paper. In Ref. [8] it was also predicted that the phenomenon should disappear when the system is heated above the (protocol-dependent) Gardner temperature. Whether or not this occurs before the shear modulus itself vanishes depends on the speed of quench from high to low temperatures. A search of a Gardner temperature would require repeating our analysis on extremely slowly quenched glasses as a way to provide a good separation of the Gardner point and the point of disappearance of the shear modulus [8]. Such an analysis is beyond the scope of the present Rapid Communication but appears to be a worthwhile endeavor for future research.

Finally, we should discuss the implications of our finding for stress-controlled experiments. Clearly, one can repeat the procedure described above at a given stress value instead of zero stress. For any given stress one can determine the mean strain, plot a stress vs strain curve, and determined the local slope. The prediction that is implied in the present Rapid Communication is that this local slope will be equivalent to the value of the shear modulus $\mu = B_1$ that can be measured from the moments of the strain fluctuations. There is no point in attempting to fit a nonlinear stress vs strain curve since the nonlinear moduli have no theoretical value. This prediction warrants a careful experimental verification.

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