

Athermal nonlinear elastic constants of amorphous solids

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We derive expressions for the lowest nonlinear elastic constants of amorphous solids in athermal conditions (up to third order), in terms of the interaction potential between the constituent particles. The effect of these constants cannot be disregarded when amorphous solids undergo instabilities such as plastic flow or fracture in the athermal limit; in such situations the elastic response increases enormously, bringing the system much beyond the linear regime. We demonstrate that the existing theory of thermal nonlinear elastic constants converges to our expressions in the limit of zero temperature. We motivate the calculation by discussing two examples in which these nonlinear elastic constants play a crucial role in the context of elastoplasticity of amorphous solids. The first example is the plasticity-induced memory that is typical to amorphous solids (giving rise to the Bauschinger effect). The second example is how to predict the next plastic event from knowledge of the nonlinear elastic constants. Using the results of our calculations we derive a simple differential equation for the lowest eigenvalue of the Hessian matrix in the external strain near mechanical instabilities; this equation predicts how the eigenvalue vanishes at the mechanical instability and the value of the strain where the mechanical instability takes place.

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I. INTRODUCTION

Many phenomena occurring in elastic materials, such as plasticity, fracture and shear banding were traditionally studied assuming that the framework of linear elasticity can be employed to describe the dynamics of the evolving systems. Recently it became clearer that this is not a good idea; close to the fracture tip, where the stress field tends to diverge, or near a plastic instability, where the shear modulus diverges toward $-\infty$, nonlinear effects become crucial if not dominant [1–3]. Moreover, recent studies indicate that nonlinear elastic moduli play an important role in the memory that amorphous solids exhibit of their loading trajectory [4]. The well known Bauschinger effect can be explained as a result of the growth of the second-order elastic modulus which is identically zero in an isotropic amorphous solid. It becomes therefore necessary to present a microscopic theory of the nonlinear elastic constants to the aim of computing them in numerical simulations. The present paper has in mind athermal quasistatic simulations, a subject of high-theoretical interest for which there had been great recent progress in understanding the range of phenomena observed, including a variety of scaling laws and the emergence of subsequent scaling theories [5–9]. Interestingly, the finite-temperature counterpart of the theory presented in this paper is available in the literature, but it is not quite obvious how to extract from it the athermal limit. We will show below that indeed the thermal theory converges to our theory when $T \rightarrow 0$.

The structure of this paper is as follows. In Sec. II, we present the derivation of the athermal elastic constants. In Sec. III, we present a brief review of the thermal elastic constants; the latter are scattered in the literature, but it is worthwhile to present them here in a compact and consistent notation. In Sec. IV, we demonstrate that the limit $T \rightarrow 0$ of the thermal elastic constants reduces properly to our results in Sec. II. Finally, in Sec. V, we demonstrate the usefulness of our results in the context of the plasticity induced memory

of amorphous solids and in predicting mechanical instabilities.

II. DERIVATION OF THE ATHERMAL NONLINEAR ELASTIC CONSTANTS

A. Definitions

We denote the ν component of the position of the i th particle as x_ν^i ; in the following Roman characters denote particle indices, and Greek characters denote Cartesian components. Given a linear transformation of coordinates $x_\nu^i \rightarrow H_{\nu\kappa} x_\kappa^i$, the resulting displacement field is $u_\nu^i = H_{\nu\kappa} x_\kappa^i - x_\nu^i$. The strain tensor is defined up to second order in the derivatives of the displacement field as

$$\epsilon_{\alpha\beta} \equiv \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\nu}{\partial x_\alpha} \frac{\partial u_\nu}{\partial x_\beta} \right), \quad (1)$$

where here and below repeated indices are summed over, unless explicitly indicated otherwise. In terms of the transformation \mathbf{H} , the strain tensor is

$$\epsilon_{\alpha\beta} \equiv \frac{1}{2} (H_{\alpha\nu}^T H_{\nu\beta} - \delta_{\alpha\beta}). \quad (2)$$

The displacement field in the definitions Eqs. (1) and (2) should be understood as taken with respect to the actual configuration, which may be *arbitrarily deformed*; the identity of the undeformed isotropic reference state is of no interest in the following derivation.

The free energy \mathcal{F} is defined in terms of the partition function \mathcal{Z} as $\mathcal{F} = -T \log \mathcal{Z}$, where

$$\mathcal{Z} = \int dp dq e^{-E/T}, \quad (3)$$

and $E = U + K$ is the sum of the potential and kinetic energies of the system; p, q are the momenta and coordinates of the

particles. We expand the free energy density \mathcal{F}/V up to a constant, again with respect to the actual configuration, in terms of this strain tensor

$$\mathcal{F}/V = \tilde{C}_1^{\alpha\beta} \epsilon_{\alpha\beta} + \frac{1}{2} \tilde{C}_2^{\alpha\beta\nu\eta} \epsilon_{\alpha\beta} \epsilon_{\nu\eta} + \frac{1}{6} \tilde{C}_3^{\alpha\beta\nu\eta\kappa\chi} \epsilon_{\alpha\beta} \epsilon_{\nu\eta} \epsilon_{\kappa\chi}, \quad (4)$$

where

$$\tilde{C}_1^{\alpha\beta} = \frac{1}{V} \left. \frac{\partial \mathcal{F}}{\partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}, \quad \tilde{C}_2^{\alpha\beta\nu\eta} = \frac{1}{V} \left. \frac{\partial^2 \mathcal{F}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\nu\eta}} \right|_{\epsilon=0},$$

$$\tilde{C}_3^{\alpha\beta\nu\eta\kappa\chi} = \frac{1}{V} \left. \frac{\partial^3 \mathcal{F}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\nu\eta} \partial \epsilon_{\kappa\chi}} \right|_{\epsilon=0}. \quad (5)$$

In the athermal limit $T \rightarrow 0$ the free energy \mathcal{F} reduces to the potential energy U , then the expansion Eq. (4) reads

$$\lim_{T \rightarrow 0} \mathcal{F}/V = U/V = C_1^{\alpha\beta} \epsilon_{\alpha\beta} + \frac{1}{2} C_2^{\alpha\beta\nu\eta} \epsilon_{\alpha\beta} \epsilon_{\nu\eta}$$

$$+ \frac{1}{6} C_3^{\alpha\beta\nu\eta\kappa\chi} \epsilon_{\alpha\beta} \epsilon_{\nu\eta} \epsilon_{\kappa\chi}, \quad (6)$$

with the coefficients

$$C_1^{\alpha\beta} = \lim_{T \rightarrow 0} \tilde{C}_1^{\alpha\beta} = \frac{1}{V} \lim_{T \rightarrow 0} \left. \frac{\partial \mathcal{F}}{\partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0},$$

$$C_2^{\alpha\beta\nu\eta} = \lim_{T \rightarrow 0} \tilde{C}_2^{\alpha\beta\nu\eta} = \frac{1}{V} \lim_{T \rightarrow 0} \left. \frac{\partial^2 \mathcal{F}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\nu\eta}} \right|_{\epsilon=0},$$

$$C_3^{\alpha\beta\nu\eta\kappa\chi} = \lim_{T \rightarrow 0} \tilde{C}_3^{\alpha\beta\nu\eta\kappa\chi} = \frac{1}{V} \lim_{T \rightarrow 0} \left. \frac{\partial^3 \mathcal{F}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\nu\eta} \partial \epsilon_{\kappa\chi}} \right|_{\epsilon=0}. \quad (7)$$

Taking the limit $T \rightarrow 0$ of free-energy derivatives is equivalent to taking the same derivatives, but of the *potential energy*, while satisfying the constraints $\mathbf{f} \equiv -\nabla U = 0$ [10]. In other words, the meaning of constrained derivatives is that *variations with ϵ keep the net forces at zero*, i.e.,

$$\frac{\partial}{\partial \epsilon} \quad \text{such that} \quad \mathbf{f} \equiv -\nabla U = 0. \quad (8)$$

We denote these constrained derivative as $\frac{\partial}{\partial \epsilon}|_f$, then

$$C_1^{\alpha\beta} = \frac{1}{V} \left. \frac{\partial U}{\partial \epsilon_{\alpha\beta}} \right|_f, \quad C_2^{\alpha\beta\nu\eta} = \frac{1}{V} \left. \frac{\partial^2 U}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\nu\eta}} \right|_{f,f},$$

$$C_3^{\alpha\beta\nu\eta\kappa\chi} = \frac{1}{V} \left. \frac{\partial^3 U}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\nu\eta} \partial \epsilon_{\kappa\chi}} \right|_{f,f,f}, \quad (9)$$

where derivatives in the above expression should be understood as taken at $\epsilon=0$. Satisfaction of the constrained derivatives is achieved by allowing for an additional displacement field \mathbf{X} to the imposed one, which we refer to as the *nonaffine* displacement field. So, upon imposing a deformation via some transformation \mathbf{H} , the total variation in coordinates can be split into a sum of two terms

$$x_\alpha^i \rightarrow H_{\alpha\beta} x_\beta^i + X_\alpha^i, \quad (10)$$

where the X_α^i 's are added to the imposed deformation to satisfy the constraint Eq. (8). The physical meaning of this procedure is that the derivatives are always computed after minimizing the energy. The original deformation brings the system away from a local minimum on the potential energy surface and the minimization amounts to an additional nonaffine displacement which must be taken into account. Note that the nonaffine field can be found explicitly [5,11], in terms of potential energy derivatives, and this is a part of the derivation below.

B. Nonaffine velocities

The constrained partial derivatives with respect to strain can be written as

$$\frac{\partial}{\partial \epsilon_{\alpha\beta}} \Big|_f = \frac{\partial}{\partial \epsilon_{\alpha\beta}} + \frac{\partial X_\nu^j}{\partial \epsilon_{\alpha\beta}} \Big|_f \frac{\partial}{\partial X_\nu^j}, \quad (11)$$

where partial derivatives with respect to strain should be understood as taken at constant \mathbf{X} , and partial derivatives with respect to coordinates should be understood as taken at constant ϵ . The quantities $\frac{\partial X_\nu^j}{\partial \epsilon_{\alpha\beta}} \Big|_f$ can be calculated by demanding that the constrained derivative of the forces vanishes, i.e., $\frac{\partial f_\kappa^i}{\partial \epsilon_{\alpha\beta}} \Big|_f = 0$. We use Eq. (11) and write

$$\frac{\partial f_\kappa^i}{\partial \epsilon_{\alpha\beta}} \Big|_f = \frac{\partial f_\kappa^i}{\partial \epsilon_{\alpha\beta}} + \frac{\partial X_\nu^j}{\partial \epsilon_{\alpha\beta}} \Big|_f \frac{\partial f_\kappa^i}{\partial X_\nu^j} = 0. \quad (12)$$

We identify the first term on the RHS of the above relation as the (negative of the) *mismatch forces* $\Xi_{\kappa\alpha\beta}^i \equiv -\frac{\partial f_\kappa^i}{\partial \epsilon_{\alpha\beta}} = -\frac{\partial^2 U}{\partial \epsilon_{\alpha\beta} \partial x_\kappa^i}$, which can be calculated explicitly from the potential energy [11]. Notice that derivatives at constant ϵ can be equivalently taken with respect to the coordinates x_α^i or the nonaffine displacements X_α^i , following Eq. (10). The mismatch forces arise due to the imposed affine deformation, before the action of nonaffine correcting displacements. The second term on the RHS of Eq. (12) contains the derivative $\frac{\partial f_\kappa^i}{\partial X_\nu^j} = -\frac{\partial^2 U}{\partial X_\nu^j \partial X_\kappa^i} \equiv -\mathcal{H}_{\kappa\nu}^{ij}$, which is the negative of the Hessian. Using these definitions of the mismatch forces and the Hessian, Eq. (12) can be rewritten as

$$\Xi_{\kappa\alpha\beta}^i + \mathcal{H}_{\kappa\nu}^{ij} \frac{\partial X_\nu^j}{\partial \epsilon_{\alpha\beta}} \Big|_f = 0. \quad (13)$$

We now define the nonaffine velocities $\mathcal{V}_{\kappa\alpha\beta}^i \equiv \frac{\partial X_\kappa^i}{\partial \epsilon_{\alpha\beta}} \Big|_f$, which can be calculated by inverting Eq. (13):

$$\mathcal{V}_{\kappa\alpha\beta}^i = \frac{\partial X_\kappa^i}{\partial \epsilon_{\alpha\beta}} \Big|_f = -(\mathcal{H}^{-1})_{\kappa\nu}^{ij} \Xi_{\nu\alpha\beta}^j. \quad (14)$$

Notice that the Hessian is not generally invertible due to zero modes that arise from the translational invariance of the potential energy [10]; to overcome this we expand the RHS of Eq. (14) in eigenfunctions of the Hessian [5]

$$\mathcal{V}_{\kappa\alpha\beta}^j = - \sum_{j,\ell} \frac{(\psi_\ell)_v^j \Xi_{v\alpha\beta}^j}{\lambda_\ell} (\psi_\ell)_\kappa^i, \quad (15)$$

where $(\psi_\ell)_v^j$ is the v component of the j th particle contribution to the ℓ th eigenfunction, λ_ℓ is the corresponding eigenvalue, and the sum over ℓ should not include the zero modes.

With the definition of the nonaffine velocities, the constrained partial derivative Eq. (11) reads

$$\left. \frac{\partial}{\partial \epsilon_{\alpha\beta}} \right|_f = \frac{\partial}{\partial \epsilon_{\alpha\beta}} + \mathcal{V}_{v\alpha\beta}^j \frac{\partial}{\partial X_\nu^i}, \quad (16)$$

which is the form that will be used from this point on.

C. Nonlinear athermal elastic constants

The third order elastic constants $C_3^{\alpha\beta\nu\eta\kappa\chi}$ are given by $\frac{1}{V} \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} \Big|_{f,f,f}$, evaluated at $\epsilon=0$; we first note that [10]

$$C_1^{\alpha\beta} = \frac{1}{V} \frac{\partial U}{\partial \epsilon_{\alpha\beta}}, \quad (17)$$

and

$$C_2^{\alpha\beta\nu\eta} = \frac{1}{V} \left(\frac{\partial^2 U}{\partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\theta v\eta}^j \Xi_{\theta\alpha\beta}^i \right). \quad (18)$$

We carry out the next order constrained derivative

$$\begin{aligned} \left. \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} \right|_{f,f,f} &= \left(\frac{\partial}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial}{\partial X_\theta^i} \right) \left(\frac{\partial^2 U}{\partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\zeta v\eta}^j \Xi_{\zeta\alpha\beta}^j \right) \\ &= \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} + \frac{\partial \mathcal{V}_{\zeta v\eta}^j \Xi_{\zeta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\zeta v\eta}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial^3 U}{\partial X_\theta^i \partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \mathcal{V}_{\zeta v\eta}^j \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i} + \mathcal{V}_{\theta\kappa\chi}^j \mathcal{V}_{\zeta v\eta}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i}. \end{aligned} \quad (19)$$

We notice now that according to Eq. (16)

$$\frac{\partial \mathcal{V}_{\zeta v\eta}^j \Xi_{\zeta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \mathcal{V}_{\zeta v\eta}^j \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i} = \left. \frac{\partial \mathcal{V}_{\zeta v\eta}^j}{\partial \epsilon_{\kappa\chi}} \right|_f \Xi_{\zeta\alpha\beta}^j. \quad (20)$$

Also $\frac{\partial^3 U}{\partial X_\theta^i \partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} = \frac{\partial \Xi_{\theta\alpha\beta}^i}{\partial \epsilon_{v\eta}} = \frac{\partial \Xi_{\theta v\eta}^i}{\partial \epsilon_{\alpha\beta}}$, with these relations, Eq. (19) becomes

$$\left. \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} \right|_{f,f,f} = \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{v\eta} \partial \epsilon_{\alpha\beta}} + \left. \frac{\partial \mathcal{V}_{\zeta v\eta}^j}{\partial \epsilon_{\kappa\chi}} \right|_f \Xi_{\zeta\alpha\beta}^j + \mathcal{V}_{\zeta v\eta}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \Xi_{\theta v\eta}^i}{\partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\theta\kappa\chi}^j \mathcal{V}_{\zeta v\eta}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i}. \quad (21)$$

The above expression requires knowledge of the quantity $\frac{\partial \mathcal{V}_{\zeta v\eta}^j}{\partial \epsilon_{\kappa\chi}} \Big|_f$ for which an explicit expression is unavailable, but can be obtained by demanding $-\frac{\partial}{\partial \epsilon_{\kappa\chi}} \Big|_f \frac{\partial f_v^j}{\partial \epsilon_{\alpha\beta}} = 0$:

$$\begin{aligned} - \left. \frac{\partial}{\partial \epsilon_{\kappa\chi}} \right|_f \frac{\partial f_v^j}{\partial \epsilon_{\alpha\beta}} &= \frac{\partial}{\partial \epsilon_{\kappa\chi}} \Big|_f (\Xi_{v\alpha\beta}^m + \mathcal{H}_{v\eta}^{mj} \mathcal{V}_{\eta\alpha\beta}^j) \\ &= \frac{\partial \Xi_{v\alpha\beta}^m}{\partial \epsilon_{\kappa\chi}} \Big|_f + \frac{\partial \mathcal{H}_{v\eta}^{mj}}{\partial \epsilon_{\kappa\chi}} \Big|_f \mathcal{V}_{\eta\alpha\beta}^j \\ &\quad + \mathcal{H}_{v\eta}^{mj} \frac{\partial \mathcal{V}_{\eta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} \Big|_f = 0. \end{aligned} \quad (22)$$

Now,

$$\left. \frac{\partial \Xi_{v\alpha\beta}^m}{\partial \epsilon_{\kappa\chi}} \right|_f = \frac{\partial \Xi_{v\alpha\beta}^m}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \Xi_{v\alpha\beta}^m}{\partial X_\theta^i},$$

$$\left. \frac{\partial \mathcal{H}_{v\eta}^{mj}}{\partial \epsilon_{\kappa\chi}} \right|_f = \frac{\partial \mathcal{H}_{v\eta}^{mj}}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \mathcal{H}_{v\eta}^{mj}}{\partial X_\theta^i}.$$

With these Eq. (22) becomes

$$\begin{aligned} \frac{\partial \Xi_{v\alpha\beta}^m}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \Xi_{v\alpha\beta}^m}{\partial X_\theta^i} + \frac{\partial \mathcal{H}_{v\eta}^{mj}}{\partial \epsilon_{\kappa\chi}} \mathcal{V}_{\eta\alpha\beta}^j + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \mathcal{H}_{v\eta}^{mj}}{\partial X_\theta^i} \mathcal{V}_{\eta\alpha\beta}^j \\ + \mathcal{H}_{v\eta}^{mj} \frac{\partial \mathcal{V}_{\eta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} \Big|_f = 0. \end{aligned} \quad (23)$$

With the identity $\frac{\partial \mathcal{H}_{v\eta}^{mj}}{\partial \epsilon_{\kappa\chi}} = \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial X_\nu^m \partial X_\eta^j} = \frac{\partial \Xi_{v\kappa\chi}^m}{\partial X_\eta^j} = \frac{\partial \Xi_{\eta\kappa\chi}^m}{\partial X_\nu^m}$, we invert Eq. (23) to get an expression for $\frac{\partial \mathcal{V}_{\eta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} \Big|_f$

$$\begin{aligned} \left. \frac{\partial \mathcal{V}_{\eta\alpha\beta}^j}{\partial \epsilon_{\kappa\chi}} \right|_f &= - (\mathcal{H}^{-1})^{jm} \left(\frac{\partial \Xi_{v\alpha\beta}^m}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \Xi_{v\alpha\beta}^m}{\partial X_\theta^i} + \mathcal{V}_{\theta\alpha\beta}^j \frac{\partial \Xi_{v\kappa\chi}^m}{\partial X_\theta^i} \right. \\ &\quad \left. + \mathcal{V}_{\theta\kappa\chi}^j \frac{\partial \mathcal{H}_{v\zeta}^{mq}}{\partial X_\theta^i} \mathcal{V}_{\zeta\alpha\beta}^q \right). \end{aligned} \quad (24)$$

Inserting this relation back in Eq. (21), together with Eq. (14) we arrive at the expression for the athermal third order elastic constants

$$\begin{aligned}
C_3^{\alpha\beta\nu\eta\kappa\chi} = & \frac{1}{V} \left[\frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\theta\alpha\beta}^j \mathcal{V}_{\zeta\nu\eta}^j \mathcal{V}_{\rho\kappa\chi}^\ell \frac{\partial^3 U}{\partial X_\theta^i \partial X_\zeta^j \partial X_\rho^\ell} \right. \\
& + \mathcal{V}_{\theta\alpha\beta}^j \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\kappa\chi}^i}{\partial X_\theta^i} + \mathcal{V}_{\theta\nu\eta}^j \mathcal{V}_{\zeta\kappa\chi}^j \frac{\partial \Xi_{\zeta\alpha\beta}^i}{\partial X_\theta^i} \\
& + \mathcal{V}_{\theta\kappa\chi}^j \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\alpha\beta}^i}{\partial X_\theta^i} + \mathcal{V}_{\zeta\alpha\beta}^j \frac{\partial \Xi_{\zeta\nu\eta}^i}{\partial \epsilon_{\kappa\chi}} + \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\kappa\chi}^i}{\partial \epsilon_{\alpha\beta}} \\
& \left. + \mathcal{V}_{\zeta\kappa\chi}^j \frac{\partial \Xi_{\zeta\alpha\beta}^i}{\partial \epsilon_{\nu\eta}} \right]. \quad (25)
\end{aligned}$$

III. THERMAL ELASTIC CONSTANTS

The derivation of the thermal elastic constants, in contrast with their athermal counterpart, can be found in the literature, see for example [11,12]. Here we provide a brief review of the thermal elastic constants up to third order.

The elastic constants at finite temperatures are given by derivatives of the free energy with respect to strain, see Eq. (5). With the expansion of the total energy $E=K+U$, K being the kinetic energy, up to third order in the strain

$$E = E_0 + E_1^{\alpha\beta} \epsilon_{\alpha\beta} + \frac{1}{2} E_2^{\alpha\beta\nu\eta} \epsilon_{\alpha\beta} \epsilon_{\nu\eta} + \frac{1}{6} E_3^{\alpha\beta\nu\eta\kappa\chi} \epsilon_{\alpha\beta} \epsilon_{\nu\eta} \epsilon_{\kappa\chi}, \quad (26)$$

and the notation $\Delta A \equiv A - \langle A \rangle$, the thermal elastic constants are

$$\begin{aligned}
\tilde{C}_1^{\alpha\beta} &= \frac{1}{V} \langle E_1^{\alpha\beta} \rangle, \quad \tilde{C}_2^{\alpha\beta\nu\eta} = \frac{1}{V} \left[\langle E_2^{\alpha\beta\nu\eta} \rangle - \frac{1}{T} \langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \rangle \right], \\
\tilde{C}_3^{\alpha\beta\nu\eta\kappa\chi} &= \frac{1}{V} \left[\langle E_3^{\alpha\beta\nu\eta\kappa\chi} \rangle + \frac{\langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \Delta E_1^{\kappa\chi} \rangle}{T^2} \right. \\
& - \frac{\langle \Delta E_1^{\alpha\beta} \Delta E_2^{\nu\eta\kappa\chi} \rangle}{T} - \frac{\langle \Delta E_1^{\nu\eta} \Delta E_2^{\alpha\beta\kappa\chi} \rangle}{T} \\
& \left. - \frac{\langle \Delta E_1^{\kappa\chi} \Delta E_2^{\alpha\beta\nu\eta} \rangle}{T} \right]. \quad (27)
\end{aligned}$$

Explicit expressions for kinetic energy derivatives with respect to strain can be found in [11].

IV. $T \rightarrow 0$ LIMIT OF THERMAL ELASTIC COEFFICIENTS

We first work out a general expression for the low-temperature expansion of the mean of any quantity $A(\mathbf{x})$, which depends only on coordinates; we start with the definition

$$\langle A \rangle = \frac{1}{\mathcal{Z}_0} \int A e^{-E/T} dp dq = \frac{1}{\mathcal{Z}_c} \int A e^{-U/T} dq, \quad (28)$$

where $\mathcal{Z}_c = \int e^{-U/T} dq$. With the notation $\delta x_\nu^i \equiv x_\nu^i - \tilde{x}_\nu^i$, we expand A around some local minimum $\tilde{\mathbf{x}}$, up to fourth order in coordinates

$$\begin{aligned}
A \simeq & A(\tilde{\mathbf{x}}) + \frac{\partial A}{\partial x_\nu^i} \Big|_{\tilde{\mathbf{x}}} \delta x_\nu^i + \frac{1}{2} \frac{\partial^2 A}{\partial x_\nu^i \partial x_\nu^j} \Big|_{\tilde{\mathbf{x}}} \delta x_\nu^i \delta x_\nu^j \\
& + \frac{1}{6} \frac{\partial^3 A}{\partial x_\zeta^\ell \partial x_\eta^j \partial x_\nu^i} \Big|_{\tilde{\mathbf{x}}} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \\
& + \frac{1}{24} \frac{\partial^4 A}{\partial x_\theta^m \partial x_\zeta^\ell \partial x_\eta^j \partial x_\nu^i} \Big|_{\tilde{\mathbf{x}}} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \delta x_\theta^m + \dots. \quad (29)
\end{aligned}$$

We now expand the potential energy up to fifth order in coordinates around the local minimum $\tilde{\mathbf{x}}$, with $T, \mathcal{M}, \mathcal{Q}$ denoting the third, fourth and fifth order derivatives of the potential energy with respect to coordinates, respectively, evaluated at $\tilde{\mathbf{x}}$:

$$\begin{aligned}
U \simeq & U(\tilde{\mathbf{x}}) + \frac{1}{2} \mathcal{H}_{\nu\eta}^{ij} \delta x_\nu^i \delta x_\eta^j + \frac{1}{6} T_{\nu\eta\zeta}^{ij\ell} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \\
& + \frac{1}{24} \mathcal{M}_{\nu\eta\zeta\theta}^{ij\ell m} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \delta x_\theta^m \\
& + \frac{1}{120} \mathcal{Q}_{\nu\eta\zeta\theta\tau}^{ij\ell mp} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \delta x_\theta^m \delta x_\tau^p, \quad (30)
\end{aligned}$$

where the first order term vanishes since $\frac{\partial U}{\partial x_\nu^i} \Big|_{\tilde{\mathbf{x}}} = 0$ for every x_ν^i . At low temperatures the virial theorem insures that the second order term in the potential energy expansion is proportional to T , hence the third, fourth and fifth order terms are of higher order in temperature; thus, in the athermal limit, we can expand the corresponding parts of the Boltzmann factor:

$$\begin{aligned}
e^{-U/T} \simeq & e^{-[U(\tilde{\mathbf{x}}) + (1/2)\mathcal{H}_{\nu\eta}^{ij} \delta x_\nu^i \delta x_\eta^j]/T} \left[1 - \frac{T_{\nu\eta\zeta}^{ij\ell} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell}{6T} \right. \\
& - \frac{\mathcal{M}_{\nu\eta\zeta\theta}^{ij\ell m} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \delta x_\theta^m}{24T} - \frac{\mathcal{Q}_{\nu\eta\zeta\theta\tau}^{ij\ell mp} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \delta x_\theta^m \delta x_\tau^p}{120T} \\
& \left. + \frac{T_{\nu\eta\zeta}^{ij\ell} T_{\theta\tau\rho}^{mpq} \delta x_\nu^i \delta x_\eta^j \delta x_\zeta^\ell \delta x_\theta^m \delta x_\tau^p \delta x_\rho^q}{72T^2} + \dots \right]. \quad (31)
\end{aligned}$$

We have omitted the other sixth-order term since it does not eventually contribute to the temperature expansion of $\langle A \rangle$. Inserting the above expansion and Eq. (29) into Eq. (28), we carry out the Gaussian integrals to obtain the low temperature approximation of the equilibrium mean of A up to terms of $\mathcal{O}(T^3)$:

$$\begin{aligned}
\langle A \rangle \simeq & A(\tilde{\mathbf{x}}) + \frac{T}{2} [\mathcal{H}^{-1} \cdot \mathcal{A}_{xx} - \mathcal{H}^{-1} \cdot \mathcal{T} \cdot \mathcal{H}^{-1} \cdot \mathcal{A}_x] \\
& + \frac{T^2}{48} [6\mathcal{H}^{-1} \cdot \mathcal{A}_{xxxx} \cdot \mathcal{H}^{-1} \\
& - 20\mathcal{H}^{-1} \cdot \mathcal{T} \cdot (\mathcal{H}^{-1} \mathcal{H}^{-1}) \cdot \mathcal{A}_{xxx} \\
& - 3\mathcal{H}^{-1} \cdot \mathcal{T} \cdot \mathcal{H}^{-1} \cdot \mathcal{A}_x \mathcal{H}^{-1} \cdot \mathcal{M} \cdot \mathcal{H}^{-1} \\
& - 6(\mathcal{H}^{-1} \mathcal{H}^{-1}) \cdot \mathcal{Q} \cdot \mathcal{H}^{-1} \cdot \mathcal{A}_x \\
& - 12\mathcal{H}^{-1} \cdot \mathcal{A}_{xx} \mathcal{H}^{-1} \cdot \mathcal{M} \cdot \mathcal{H}^{-1}
\end{aligned}$$

$$-40(\mathcal{H}^{-1} \cdot \mathcal{T}) \cdot (\mathcal{H}^{-1} \cdot \mathcal{T} \cdot \mathcal{H}^{-1})(\mathcal{H}^{-1} \cdot \mathcal{A}_{xx}), \quad (32)$$

where \mathcal{A}_x , \mathcal{A}_{xx} etc. denote the tensors of first, second etc. derivatives of A with respect to \mathbf{x} . Using this expression, we derive relations for fluctuations. Assume that also B and C are functions of coordinates \mathbf{x} ; with the definition $\Delta A = A - \langle A \rangle$, we have

$$\frac{\langle \Delta A \Delta B \rangle}{T} \simeq \frac{1}{2} [\mathcal{A}_x \cdot \mathcal{H}^{-1} \cdot \mathcal{B}_x + \mathcal{B}_x \cdot \mathcal{H}^{-1} \cdot \mathcal{A}_x] + \mathcal{O}(T), \quad (33)$$

and

$$\begin{aligned} \frac{\langle \Delta A \Delta B \Delta C \rangle}{T^2} \simeq & \mathcal{H}^{-1} \cdot \mathcal{A}_x \cdot \mathcal{C}_{xx} \cdot \mathcal{H}^{-1} \cdot \mathcal{B}_x \\ & + \mathcal{H}^{-1} \cdot \mathcal{B}_x \cdot \mathcal{A}_{xx} \cdot \mathcal{H}^{-1} \cdot \mathcal{C}_x \\ & + \mathcal{H}^{-1} \cdot \mathcal{C}_x \cdot \mathcal{B}_{xx} \cdot \mathcal{H}^{-1} \cdot \mathcal{A}_x - (\mathcal{H}^{-1} \cdot \mathcal{A}_x) \\ & \times (\mathcal{H}^{-1} \cdot \mathcal{B}_x)(\mathcal{H}^{-1} \cdot \mathcal{C}_x) \cdot \mathcal{T} + \mathcal{O}(T). \end{aligned} \quad (34)$$

In this section we will make use of the following definitions:

$$\begin{aligned} U_0 &\equiv U(\epsilon=0), \quad U_1^{\alpha\beta} \equiv \left. \frac{\partial U}{\partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}, \\ U_2^{\alpha\beta\nu\eta} &\equiv \left. \frac{\partial^2 U}{\partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}, \\ U_3^{\alpha\beta\nu\eta\kappa\chi} &\equiv \left. \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}, \\ K_0 &\equiv K(\epsilon=0), \quad K_1^{\alpha\beta} \equiv \left. \frac{\partial K}{\partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}, \\ K_2^{\alpha\beta\nu\eta} &\equiv \left. \frac{\partial^2 K}{\partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}, \\ K_3^{\alpha\beta\nu\eta\kappa\chi} &\equiv \left. \frac{\partial^3 K}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}, \\ E_0 &\equiv U_0 + K_0, \quad E_1^{\alpha\beta} \equiv U_1^{\alpha\beta} + K_1^{\alpha\beta}, \\ E_2^{\alpha\beta\nu\eta} &\equiv U_2^{\alpha\beta\nu\eta} + K_2^{\alpha\beta\nu\eta}, \\ E_3^{\alpha\beta\nu\eta\kappa\chi} &\equiv U_3^{\alpha\beta\nu\eta\kappa\chi} + K_3^{\alpha\beta\nu\eta\kappa\chi}. \end{aligned} \quad (35)$$

A. First-order elastic constants—athermal limit

The first order free energy derivative with respect to strain is given by [see Eq. (27)]

$$\frac{\partial \mathcal{F}}{\partial \epsilon_{\alpha\beta}} = \langle E_1^{\alpha\beta} \rangle = \langle U_1^{\alpha\beta} + K_1^{\alpha\beta} \rangle = \langle U_1^{\alpha\beta} \rangle + \langle K_1^{\alpha\beta} \rangle. \quad (36)$$

In the athermal limit the kinetic term vanishes and following relation Eq. (32) we are left with

$$\lim_{T \rightarrow 0} \langle E_1^{\alpha\beta} \rangle = \lim_{T \rightarrow 0} \langle U_1^{\alpha\beta} \rangle = \left. \frac{\partial U}{\partial \epsilon_{\alpha\beta}} \right|_{\bar{x}}. \quad (37)$$

From here the athermal limit of the first order elastic constants is

$$\lim_{T \rightarrow 0} \tilde{C}_1^{\alpha\beta} = \frac{1}{V} \left. \frac{\partial U}{\partial \epsilon_{\alpha\beta}} \right|_{\bar{x}}, \quad (38)$$

in agreement with Eq. (17).

B. Second-order elastic constants—athermal limit

The second order free-energy derivative with respect to strain is given by [see Eq. (27)]

$$\frac{\partial^2 \mathcal{F}}{\partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} = \langle E_2^{\alpha\beta\nu\eta} \rangle - \frac{1}{T} \langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \rangle. \quad (39)$$

The first term is $\langle E_2^{\alpha\beta\nu\eta} \rangle = \langle U_2^{\alpha\beta\nu\eta} \rangle + \langle K_2^{\alpha\beta\nu\eta} \rangle$; in the athermal limit the kinetic term vanishes, and following Eq. (32) we are left with

$$\lim_{T \rightarrow 0} \left\langle \frac{\partial^2 U}{\partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right\rangle = \left. \frac{\partial^2 U}{\partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right|_{\bar{x}}. \quad (40)$$

The second term in Eq. (39) is

$$\frac{\langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \rangle}{T} = \frac{\langle \Delta U_1^{\alpha\beta} \Delta U_1^{\nu\eta} \rangle + \langle \Delta K_1^{\alpha\beta} \Delta K_1^{\nu\eta} \rangle}{T},$$

since all mixed terms involving products of kinetic energy and potential energy derivatives cancel. The second term of the RHS of the above relation is proportional to T^2 , so we are left with

$$\lim_{T \rightarrow 0} \frac{1}{T} \langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \rangle = \lim_{T \rightarrow 0} \frac{1}{T} \langle \Delta U_1^{\alpha\beta} \Delta U_1^{\nu\eta} \rangle.$$

Using the relation Eq. (33) and definition Eq. (14), we obtain

$$\begin{aligned} \lim_{T \rightarrow 0} \frac{1}{T} \langle \Delta U_1^{\alpha\beta} \Delta U_1^{\nu\eta} \rangle &= \frac{1}{2} [\Xi_{\kappa\alpha\beta}^i (\mathcal{H}^{-1})_{\kappa\chi}^{ij} \Xi_{\chi\nu\eta}^j \\ &+ \Xi_{\kappa\nu\eta}^i (\mathcal{H}^{-1})_{\kappa\chi}^{ij} \Xi_{\chi\alpha\beta}^j] = -\mathcal{V}_{\chi\alpha\beta}^j \Xi_{\chi\nu\eta}^i. \end{aligned} \quad (41)$$

Finally

$$\lim_{T \rightarrow 0} \tilde{C}_2^{\alpha\beta\nu\eta} = \frac{1}{V} \left[\left. \frac{\partial^2 U}{\partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right|_{\bar{x}} + \mathcal{V}_{\chi\alpha\beta}^j \Xi_{\chi\nu\eta}^i \right] \quad (42)$$

in agreement with Eq. (18).

C. Third-order elastic constants—athermal limit

The third-order free-energy derivative with respect to strain is given by [see Eq. (27)]

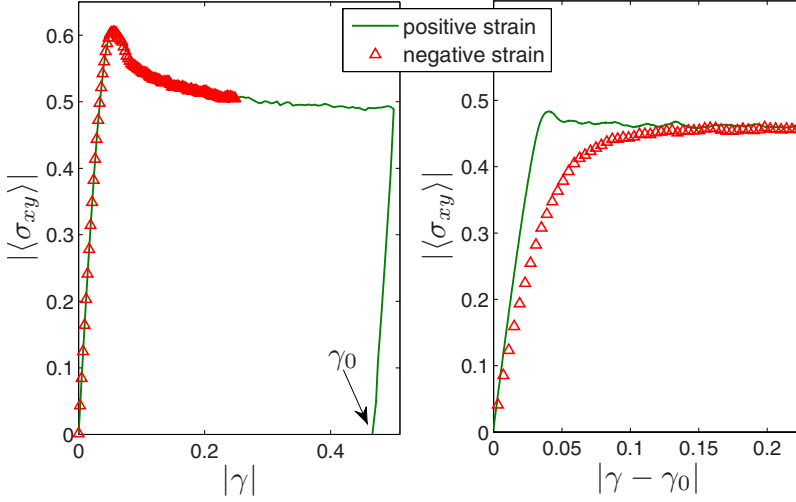


FIG. 1. (Color online) Stress-strain curves. Left panel: starting the experiment from a freshly prepared sample results in a symmetric trajectory for $\gamma \rightarrow -\gamma$. Right panel: starting the experiment from the zero-stress state with $\gamma = \gamma_0$ results in an asymmetric trajectory, see text for details. Data was averaged over 500 independent stress-strain curves at $T=0.01$ where temperature is measured in units of ε/k_B , see [4] for details

$$\begin{aligned} \frac{\partial^3 \mathcal{F}}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} &= \langle E_3^{\alpha\beta\nu\eta\kappa\chi} \rangle + \frac{\langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \Delta E_1^{\kappa\chi} \rangle}{T^2} \\ &\quad - \frac{\langle \Delta E_1^{\alpha\beta} \Delta E_2^{\nu\eta\kappa\chi} \rangle}{T} - \frac{\langle \Delta E_1^{\nu\eta} \Delta E_2^{\alpha\beta\kappa\chi} \rangle}{T} \\ &\quad - \frac{\langle \Delta E_1^{\kappa\chi} \Delta E_2^{\alpha\beta\nu\eta} \rangle}{T}. \end{aligned} \quad (43)$$

The first term on the RHS of Eq. (43) is $\langle E_3^{\alpha\beta\nu\eta\kappa\chi} \rangle = \langle U_3^{\alpha\beta\nu\eta\kappa\chi} \rangle + \langle K_3^{\alpha\beta\nu\eta\kappa\chi} \rangle$; in the athermal limit the kinetic term vanishes, and following Eq. (32) we are left with

$$\lim_{T \rightarrow 0} \left\langle \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right\rangle = \left. \frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right|_{\bar{x}}. \quad (44)$$

The second term in Eq. (43) is

$$\begin{aligned} &\frac{\langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \Delta E_1^{\kappa\chi} \rangle}{T^2} \\ &= \frac{\langle \Delta U_1^{\alpha\beta} \Delta U_1^{\nu\eta} \Delta U_1^{\kappa\chi} \rangle + \langle \Delta K_1^{\alpha\beta} \Delta K_1^{\nu\eta} \Delta K_1^{\kappa\chi} \rangle}{T^2}, \end{aligned} \quad (45)$$

since similarly to the second-order athermal limit case, all mixed terms cancel. The triple product $\langle \Delta K_1^{\alpha\beta} \Delta K_1^{\nu\eta} \Delta K_1^{\kappa\chi} \rangle \sim T^3$, so we are left with

$$\lim_{T \rightarrow 0} \frac{\langle \Delta E_1^{\alpha\beta} \Delta E_1^{\nu\eta} \Delta E_1^{\kappa\chi} \rangle}{T^2} = \lim_{T \rightarrow 0} \frac{\langle \Delta U_1^{\alpha\beta} \Delta U_1^{\nu\eta} \Delta U_1^{\kappa\chi} \rangle}{T^2}.$$

Using relation Eq. (34) and definition Eq. (14), this is

$$\begin{aligned} &\lim_{T \rightarrow 0} \frac{\langle \Delta U_1^{\alpha\beta} \Delta U_1^{\nu\eta} \Delta U_1^{\kappa\chi} \rangle}{T^2} \\ &= \mathcal{V}_{\theta\alpha\beta}^j \mathcal{V}_{\zeta\nu\eta}^j \mathcal{V}_{\rho\kappa\chi}^\ell T_{\theta\zeta\rho}^{j\ell} + \mathcal{V}_{\theta\alpha\beta}^j \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\kappa\chi}^j}{\partial X_\theta^i} \\ &\quad + \mathcal{V}_{\theta\nu\eta}^j \mathcal{V}_{\zeta\kappa\chi}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i} + \mathcal{V}_{\theta\kappa\chi}^j \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i}. \end{aligned} \quad (46)$$

Finally, we use relation Eq. (33) for the remaining terms:

$$\lim_{T \rightarrow 0} \frac{\langle \Delta E_1^{\alpha\beta} \Delta E_2^{\nu\eta\kappa\chi} \rangle}{T} = \lim_{T \rightarrow 0} \frac{\langle \Delta U_1^{\alpha\beta} \Delta U_2^{\nu\eta\kappa\chi} \rangle}{T} = -\mathcal{V}_{\zeta\alpha\beta}^i \frac{\partial \Xi_{\zeta\nu\eta}^i}{\partial \epsilon_{\kappa\chi}}. \quad (47)$$

Combining results Eqs. (44), (46), and (47), we arrive at the final result

$$\begin{aligned} \lim_{T \rightarrow 0} \tilde{C}_3^{\alpha\beta\nu\eta\kappa\chi} &= \frac{1}{V} \left[\frac{\partial^3 U}{\partial \epsilon_{\kappa\chi} \partial \epsilon_{\nu\eta} \partial \epsilon_{\alpha\beta}} \right. \\ &\quad + \mathcal{V}_{\theta\alpha\beta}^j \mathcal{V}_{\zeta\nu\eta}^j \mathcal{V}_{\rho\kappa\chi}^\ell \frac{\partial^3 U}{\partial X_\theta^i \partial X_\zeta^j \partial X_\rho^\ell} \\ &\quad + \mathcal{V}_{\theta\alpha\beta}^j \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\kappa\chi}^j}{\partial X_\theta^i} + \mathcal{V}_{\theta\nu\eta}^j \mathcal{V}_{\zeta\kappa\chi}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i} \\ &\quad + \mathcal{V}_{\theta\kappa\chi}^j \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial X_\theta^i} + \mathcal{V}_{\zeta\alpha\beta}^j \frac{\partial \Xi_{\zeta\nu\eta}^j}{\partial \epsilon_{\kappa\chi}} \\ &\quad \left. + \mathcal{V}_{\zeta\nu\eta}^j \frac{\partial \Xi_{\zeta\kappa\chi}^j}{\partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\zeta\kappa\chi}^j \frac{\partial \Xi_{\zeta\alpha\beta}^j}{\partial \epsilon_{\nu\eta}} \right]. \end{aligned} \quad (48)$$

in agreement with Eq. (25).

V. EXAMPLES OF APPLICATIONS

To justify and motivate the calculation of the nonlinear elastic constants we present now two examples of important issues regarding elastoplastic behavior in amorphous solids that cannot be discussed without invoking these nonlinear constants. The first is plasticity-induced anisotropy and the second is the predictions of plastic failure.

A. Plasticity-induced anisotropy

A freshly produced amorphous solid is isotropic, and as such presents a symmetric stress vs strain curve for positive or negative strain. This is not the case for the same amorphous solid after it had been already strained such that its stress exceeded its yield stress where plastic deformations become numerous [14,15]. This is demonstrated in Fig. 1. A typical averaged stress-strain curve for a model amorphous

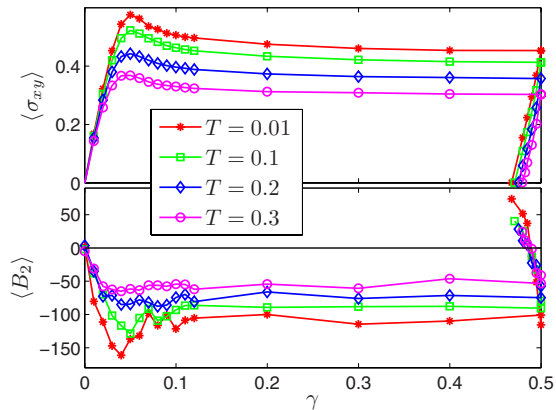


FIG. 2. (Color online) Upper panel: Trajectories of stress vs strain for four different temperature at the same strain rate $\dot{\gamma} = 10^{-4}$. Lower panel: the corresponding values of $\langle B_2 \rangle$ as a function of strain. Data was averaged over 1000 independent stress-strain curves at each temperature. Note that $\langle B_2 \rangle$ is negative even when the averaged stress-strain curve has a positive curvature, see text for discussion.

solid (see Ref. [4]. for numerical details) starting from an ensemble of freshly prepared homogenous states is shown in the left panel, with a symmetric trajectory for positive or negative shear strain. Once in the steady flow state, each system in the ensemble is brought back to a zero-stress state, which serves as the starting point for a second experiment in which a positive and negative strain is put on the system as shown in the right panel of Fig. 1. Even though the initial ensemble is prepared to have zero mean stress, the average trajectory is now asymmetric. This phenomenon, sometime referred to as the Bauschinger effect [13], shows that the starting point γ_0 for the second experiment (referred below as the Bauschinger point) retains a memory of the loading history in some form of anisotropy.

To shed light on the anisotropy of the Bauschinger point we choose to measure the sum

$$B_2(\gamma^*) \equiv \lim_{T \rightarrow 0} [3\tilde{C}_2^{\text{xyyy}} + \tilde{C}_3^{\text{xyxyxy}}] = \lim_{T \rightarrow 0} \left. \frac{d^2 \sigma_{xy}}{d\gamma^2} \right|_{\gamma=\gamma^*}, \quad (49)$$

which can be determined using the results Eqs. (18) and (25). In particular we note that $\langle B_2 \rangle$ is identically zero in an isotropic ensemble. It gains a nonzero value when plastic events take place and begin to build anisotropy. In Fig. 2, we present results of numerical simulations in a typical model of an amorphous solid (for details cf. [4]), and present the measured value of $\langle B_2 \rangle$ along the trajectory shown in Fig. 1. In addition to the very low temperature trajectory in Fig. 1 we show also measurements of $\langle B_2 \rangle$ for simulations performed at other three different temperatures. For all these trajectories B_2 was measured by quenching to zero temperature configurations sampled along the thermal trajectory. The magnitude of the Bauschinger effect goes down when temperature goes up, and this is in good agreement with the value of $\langle B_2 \rangle$ at the Bauschinger point which also decreases when temperature increases. We thus see that the values of the nonlinear elastic constants can serve as natural measures for the degree

of anisotropy that is built up in an amorphous solid due to plastic deformations. Further discussion of this measure can be found in [4]. Note that in [4] the value of B_2 was obtained directly from stress vs. strain curves, computing the derivatives numerically. With the results obtained in this paper we can compute B_2 or any other elastic constant directly from the particle interactions. This will open up in the future a possibility to define local values of the elastic constants, providing maps of B_2 or other nonlinear elastic constants.

B. Predicting plasticity

Imagine an amorphous solid under a given state of strain. Can one predict how much additional strain is needed to reach plastic failure? Recently we have shown, cf. [3], that an accurate predictor of plastic failure in an amorphous solid can be constructed with the help of the higher order derivatives of the potential function. Our findings not only offer a predictive tool for the onset of failure, but also point out the importance of nonlinearities, and in particular those that couple nonlinearly “softening” regions with strain at larger scales. It is indeed this nonlinear interaction which produces a reinforcing mechanism leading ultimately to a catastrophic event in the form of plastic yielding.

To fix ideas, imagine a simple shear deformation applied to a given piece of amorphous solid [for simplicity in two dimensional (2D), with immediate extensions to three dimensional (3D)]. A small strain increment $\delta\gamma$ corresponds to a change of the i th particle positions $\mathbf{x}_i \rightarrow \mathbf{x}'_i$ as

$$x'_i = x_i + \delta\gamma y_i,$$

$$y'_i = y_i.$$

In athermal quasistatic conditions ($T \rightarrow 0$, $\dot{\gamma} \rightarrow 0$), the system lives in local minima, and follows strain-induced changes of the potential energy surface. Therefore, the particles do not follow homogeneously the macroscopic strain, and their positions change as $\mathbf{x}_i \rightarrow \mathbf{x}'_i + \mathbf{X}_i$, where \mathbf{X}_i denotes nonaffine displacements. Around some stable reference state at $\gamma = \gamma^*$, the field \mathbf{X}_i , the system energy, and internal stress σ_{xy} are smooth functions of γ . We can thus write:

$$\sigma_{xy}(\gamma) = \sum_{n=0}^{\infty} \frac{B_n}{n!} (\gamma - \gamma^*)^n, \quad B_n = \lim_{T \rightarrow 0} \left. \frac{d^n \sigma_{xy}}{d\gamma^n} \right|_{\gamma=\gamma^*}. \quad (50)$$

As the strain increases, the system must eventually lose mechanical stability; the “elastic branch” on the stress curve ends in a discontinuity as the system fails via a first subsequent “plastic event.” It is precisely at this instability, say at $\gamma = \gamma_p$, that the function $\sigma_{xy}(\gamma)$ loses its analyticity. Accordingly we recognize that the radius of convergence of the series Eq. (50) is precisely $|\gamma_p - \gamma^*|$, where γ_p can be larger or smaller than γ^* .

Mechanical instabilities are associated with the vanishing of an eigenvalue of the Hessian, which we will denote as λ_p . Here, as opposed to the analysis of [3,5], we do not make any assumptions about the functional form of $\lambda_p(\gamma)$. The vanishing of λ_p implies that any terms of the elastic constants that are composed of the inverse of the Hessian \mathcal{H}^{-1}

will diverge at λ_p ; hence, the strongest diverging terms are those which are composed of the largest number of \mathcal{H}^{-1} 's. Accordingly, higher order elastic constants will consist of stronger divergences, as can be understood, for example, by comparing Eq. (18) with Eq. (25). Near γ_p the most diverging terms will dominate over the rest, so we will consider in the following analysis the most diverging terms of each order of the athermal elastic constants.

We begin with $B_1 = C_1^{yy} + C_2^{xyxy}$, which are given by Eqs. (17) and (18); following the discussion above, the most (and only, for B_1) diverging term is $V_{\theta xy}^i \Xi_{\theta xy}^i / V$ [recall that \mathcal{V} consists of \mathcal{H}^{-1} , see Eqs. (14) and (15)]. Close to γ_p , the diverging term will dominate, so we can write

$$B_1 \sim \frac{1}{\lambda_p}. \quad (51)$$

We continue with B_2 ; the most diverging term in B_2 is the most diverging term in C_3^{xyxyxy} ; from Eq. (25), this is

$$B_2 \sim \mathcal{V}_{\theta xy}^i \mathcal{V}_{\xi xy}^j \mathcal{V}_{\rho xy}^\ell \mathcal{T}_{\theta \xi \rho}^{ij\ell} \sim \frac{1}{\lambda_p^3}. \quad (52)$$

Since $B_2 \equiv \frac{dB_1}{d\gamma}$, we obtain a differential equation for $\lambda_p(\gamma)$:

$$\frac{1}{\lambda_p^3} \sim \frac{d}{d\gamma} \left(\frac{1}{\lambda_p} \right) = -\frac{1}{\lambda_p^2} \frac{d\lambda_p}{d\gamma}.$$

We rewrite this as

$$\frac{d\lambda_p}{d\gamma} \sim -\frac{1}{\lambda_p}, \quad (53)$$

for which, together with the boundary condition $\lambda_p|_{\gamma_p} = 0$, the solution is

$$\lambda_p \sim \sqrt{\gamma_p - \gamma}, \quad (54)$$

in agreement with [3,5].

With this result, we are able to derive expressions for the diverging terms of B_3 and B_4 , as a function of γ_p ; starting from $B_1 = \frac{a}{\sqrt{\gamma_p - \gamma}}$ we obtain the relations

$$B_3 \approx \frac{3a}{4(\gamma_p - \gamma)^{5/2}} \quad \text{and} \quad B_4 \approx \frac{15a}{8(\gamma_p - \gamma)^{7/2}}. \quad (55)$$

Solving for γ_p , we obtain the prediction

$$\gamma_p = \gamma + \frac{5B_3}{2B_4}, \quad (56)$$

where the most diverging terms of B_3 and B_4 should be considered. Notice that one could, in principle derive expressions for γ_p involving lower order elastic constants; see [3] for discussion.

We finally derive expressions for the most diverging terms of B_3 and B_4 ; starting from the most diverging term in C_3 , we take another constrained derivative:

$$\begin{aligned} \frac{\partial}{\partial \epsilon} ([\mathcal{V}\mathcal{V}\mathcal{V}] \cdot \mathcal{T}) \Big|_f &= -[\mathcal{T} \cdot \mathcal{V}\mathcal{V}] \cdot \mathcal{H}^{-1} \cdot [\mathcal{T} \cdot \mathcal{V}\mathcal{V}] \\ &+ 2 \text{ symmetric terms,} \end{aligned} \quad (57)$$

where here and in the following, the contractions are *only* over indices and components of particle coordinates, and we only consider here the most diverging term of $\frac{\partial \mathcal{V}}{\partial \epsilon} \Big|_f$; see Eq. (24).

Taking another constrained derivative of Eq. (57) requires an expression for $\frac{\partial(\mathcal{H}^{-1})_{ij}^{\alpha\beta}}{\partial \epsilon_{\nu\eta}} \Big|_f$, which can be obtained by applying the rule Eq. (16) on $\mathcal{H}^{-1} \cdot \mathcal{H}$:

$$\begin{aligned} \frac{\partial(\mathcal{H}^{-1})_{ij}^{\alpha\beta}}{\partial \epsilon_{\alpha\beta}} \Big|_f \mathcal{H}_{\eta\kappa}^{j\ell} + (\mathcal{H}^{-1})_{ij}^{\alpha\beta} \frac{\partial \mathcal{H}_{\eta\kappa}^{j\ell}}{\partial \epsilon_{\alpha\beta}} \Big|_f &= \frac{\partial(\mathcal{H}^{-1})_{ij}^{\alpha\beta}}{\partial \epsilon_{\alpha\beta}} \Big|_f \mathcal{H}_{\eta\kappa}^{j\ell} \\ + (\mathcal{H}^{-1})_{ij}^{\alpha\beta} \left(\frac{\partial \mathcal{H}_{\eta\kappa}^{j\ell}}{\partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\tau\alpha\beta}^n \mathcal{T}_{\tau\eta\kappa}^{mj\ell} \right) &= 0. \end{aligned}$$

From here

$$\frac{\partial(\mathcal{H}^{-1})_{ij}^{\alpha\beta}}{\partial \epsilon_{\alpha\beta}} \Big|_f = -(\mathcal{H}^{-1})_{i\ell}^{\alpha\beta} \left(\frac{\partial \mathcal{H}_{\kappa\chi}^{\ell m}}{\partial \epsilon_{\alpha\beta}} + \mathcal{V}_{\tau\alpha\beta}^n \mathcal{T}_{\tau\kappa\chi}^{\ell m} \right) (\mathcal{H}^{-1})_{\chi\eta}^{mj}. \quad (58)$$

With this relation and Eq. (24), we carry out another constrained derivative of Eq. (57), keeping only the most diverging terms

$$\begin{aligned} -\frac{\partial}{\partial \epsilon} [(\mathcal{T} \cdot \mathcal{V}\mathcal{V}) \cdot \mathcal{H}^{-1} \cdot (\mathcal{T} \cdot \mathcal{V}\mathcal{V})] \Big|_f \\ = \mathcal{T} \cdot \{ [\mathcal{H}^{-1} \cdot (\mathcal{T} \cdot \mathcal{V}\mathcal{V})] \mathcal{V} [\mathcal{H}^{-1} \cdot (\mathcal{T} \cdot \mathcal{V}\mathcal{V})] \} \\ + 14 \text{ symmetric terms.} \end{aligned}$$

This leads us to the final expression for the instability strain γ_p :

$$\gamma_p = \gamma_0$$

$$= \frac{1}{2} \frac{(\mathcal{T} \cdot \mathcal{V}_{xy} \mathcal{V}_{xy}) \cdot \mathcal{H}^{-1} \cdot (\mathcal{T} \cdot \mathcal{V}_{xy} \mathcal{V}_{xy})}{\mathcal{T} \cdot \{ [\mathcal{H}^{-1} \cdot (\mathcal{T} \cdot \mathcal{V}_{xy} \mathcal{V}_{xy})] \mathcal{V}_{xy} [\mathcal{H}^{-1} \cdot (\mathcal{T} \cdot \mathcal{V}_{xy} \mathcal{V}_{xy})] \}}. \quad (59)$$

Notice that the above expression for γ_p can be calculated numerically by solving two linear equations; first, for \mathcal{V} using Eq. (14). With the solution for \mathcal{V} in hand, one can then solve Eq. (23) for $\frac{\partial \mathcal{V}}{\partial \epsilon} \Big|_f \approx \mathcal{H}^{-1} \cdot (\mathcal{T} \cdot \mathcal{V}\mathcal{V})$. How these predic-

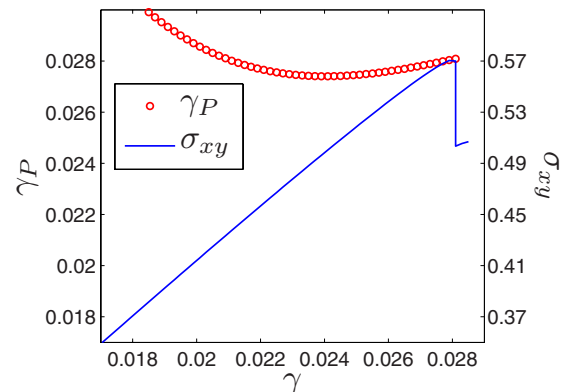


FIG. 3. (Color online) Typical stress vs strain curve shown up to the plastic event, (scale to the right) and the predicted γ_p as a function of γ .

tions work in practice can be read in [3]. Here, we provide an example of the prediction of γ_P in Fig. 3 for the same amorphous solid treated above.

VI. SUMMARY AND CONCLUSIONS

In this paper, we derived closed-form expressions for the nonlinear elastic constants of amorphous solids up to third order. We presented both the thermal and the athermal theory, and demonstrated that the latter is obtained as a limit of the former when $T \rightarrow 0$. The expressions derived above should be useful in numerical simulations where knowledge of these nonlinear constants is indispensable due to the high values of the stresses obtained near mechanical instabilities. In particular these expressions will allow extension of the

evaluation of these objects to local coarse-grained fields. Such an extension will be presented in a forthcoming article. We demonstrated the use of these nonlinear objects in the context of understanding the plasticity-induced anisotropy that arises in amorphous solids after a straining trajectory and in predicting the plastic failure of amorphous solids to increasing strain.

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