Comparison of the Helmholtz, Gibbs, and Collective-modes methods to obtain nonaffine elastic constants

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We review and compare the Born-Huang and the Lemaitre-Maloney’s theories that lead to analytical expressions for elastic constants, accounting for affine and nonaffine deformations in a lattice. The Born-Huang method is based on Helmholtz energy while the Lemaitre-Maloney’s formalism focus on Gibbs force. Although starting from different perspectives, in the linear elastic limit, and in equilibrium, elastic material constants must be the same in all these methods. This is explicitly verified on examples of linear chains, and numerical simulation of a non-centrosymmetric crystal.

I. INTRODUCTION

It is manifest that elastic materials experience internal resistance to the deformation caused by external forces. They tend to return to original sizes and shapes when the external influence is eliminated. The elasticity of materials is generally described by a stress-strain curve, which exhibits a characteristic linear region for sufficiently small deformations. This linear regime is vital for, e.g. elastic waves, and most elastic theories are established in this linear regime. In a one-dimensional rod, the simplest linear relation between stress and strain is known as Hooke’s law; in three dimensions, the general proportionality between stress and strain is a 4th-rank tensor of stiffness coefficient \cite{1}.

At zero temperature, once the relative initial positions of atoms are known, it is then a simple task to add all contributing interactions to elastic constants for homogeneous (affine) deformations. The resultant elastic constants are often called affine. When the two assumptions, zero temperature and homogeneous displacements, are not valid, one needs to develop a more complicated theory of nonaffinity (local, inhomogeneous). Early works focus on thermal effects on elasticity in crystals \cite{2,3}. In recent decades, athermal systems, like granular materials or foams, raise a lot of attention, investigating nonaffine elastic constants \cite{4–8}. In other words, even at zero temperature, particles (atoms) do not always follow homogeneous displacement fields. They instead attempt to minimize the potential energy of the system, and in some cases, this requires additional local nonaffine displacements, no matter how small deformation the system is strained to. The nonaffine correction to the elastic constants can be prominent, which has been found in simulation of a non-centrosymmetric lattice \cite{9}.

The formal expressions for the nonaffine corrections were systematically developed by Lemaitre and Maloney (LM) via studying the (Gibbs) force acting on each particle in the system \cite{10}. Through performing normal mode decomposition, their analysis relates nonaffine corrections to the correlator of a fluctuating force field, which can be extended to the viscoelastic dynamical response of the system.

Prior to LM, the linear elastic constants were studied in detail in Born and Huang’s (BH’s) work. The most familiar BH results are for the basic affine elastic constants, although they have actually discussed the nonaffine deformation case in great detail (but not yet derived complete analytical expressions for nonaffine corrections) \cite{11}. However, reviewing the BH theory, and comparing it with LM formalism, we find that they actually attack the elasticity problem from two complementary angles: LM formalism works by identifying the local nonaffine forces, while BH approaches are based on local nonaffine displacements (Helmholtz), which are conjugate to each other. Last but not least, in long-range (short wavelength) regime, the vibrational lattice wave from collective motions are entangled with the elastic wave propagating inside the lattice, which provides an additional path to elastic constants.

This paper is organised as follows: Section II reviews three approaches to elastic constants, including their interpretations of both affine and nonaffine contributions. Section III begins with clarifying the link between Gibbs and Helmholtz’s interpretations, with supporting examples of 1D linear lattices and a non-centrosymmetric crystal, where we compare in detail ways of calculating elastic constants. Finally, in Section IV, we draw our conclusions and give an insight of practical applications of these methods.

II. REVIEW OF DIFFERENT APPROACHES TO ELASTIC CONSTANTS

A. BH: elastic constants for non-ionic crystals

We take into account homogeneous deformation in a small neighborhood of \( R^0 \):

\[
s^\mu(R^0 + \delta R) = s^\mu(R^0) + \sum_\nu \frac{\partial s^\mu}{\partial R^\nu} \delta R^\nu \quad (1)
\]

The first term on the RHS represents the translation of the small region as a whole while the last term is the
elastic deformation. In lattice, particle (nucleus) \( I \) lies in cell \( l \) has displacement \( s^I_l(l) \). Eq. (1) is then equivalent to

\[
s^I_l(l) = s^I_l + \sum_\nu \frac{\partial s^\nu}{\partial R^\nu} R^\nu_l(l) \tag{2}
\]

where \( s^I_l \) is the additional displacement all particles of each type has to elastic deformation. From this, we have

\[
U = \frac{1}{2} \sum_{I,J,\mu,\nu} \left\{ \frac{I}{\mu} \frac{J}{\nu} \right\} s^I_l s^J_l + \sum_{I,J,\mu,\xi,\eta} \left\{ \frac{I}{\mu} \frac{J}{\eta} \right\} s^I_l s^J_l \eta_{\mu\xi} + \frac{1}{2} \sum_{\nu,\mu,\xi,\eta} \{\nu\mu\xi\eta\} s^\nu \eta_{\mu\xi} \tag{3}
\]

Denoting (external) symmetric strain \( \eta \) by

\[
\eta_{\mu\nu} = \eta_{\nu\mu} = \frac{1}{2} \left( \frac{\partial s^\mu}{\partial R^\nu} + \frac{\partial s^\nu}{\partial R^\mu} \right)
\]

The energy density \( U \) is rewritten as

\[
U = \frac{1}{2} \sum_{I,J,\mu,\nu} \left\{ \frac{I}{\mu} \frac{J}{\nu} \right\} s^I_l s^J_l + \sum_{I,J,\mu,\xi,\eta} \left\{ \frac{I}{\mu} \frac{J}{\eta} \right\} s^I_l \eta_{\mu\xi} + \frac{1}{2} \sum_{\nu,\mu,\xi,\eta} \{\nu\mu\xi\eta\} s^\nu \eta_{\mu\xi}
\]

Physically, \( s^\mu_I \) is known as (internal) nonaffine displacement such that the energy density becomes minimum for the given external elastic strain components \( \eta_{\mu\nu} \). That is

\[
0 = \frac{\partial U}{\partial s^I_l} = \sum_{J,\nu} \left\{ \frac{I}{\mu} \frac{J}{\nu} \right\} s^J_l + \sum_{\xi} \left\{ \frac{I}{\nu} \frac{\xi}{\eta} \right\} \eta_{\nu\xi} \tag{6}
\]

which gives \((N-1)d\) independent equations. The solutions \( s^I_l(\eta) \) of these mechanical equilibrium conditions are, in fact, the nonaffine displacements. Since the energy density depends only on the differences between the different \( s^I_l \). Without loss of generality, we can let \( s^I_l = 0 \). When the internal displacements are eliminated, the energy density becomes a quadratic expression in \( \eta \), whose coefficient \{\nu\mu\xi\eta\} will receive a correction after solving for \( s^I_l \), which we write as \{\nu\mu\xi\eta\}'. The detailed analysis of resultant correction to elastic constant is shown in

\[
s^I_j(l') - s^I_j(0) = s^I_j - s^I_j + \sum_\nu \left( \partial s^\nu / \partial R^\nu \right) R^\nu_j(l') \tag{7}
\]

By \( R^\nu_j(l') \), we mean \( R^\nu_j(l') - R^\nu_j(0) \). In general, there are \( N \) particles in each cell and \( d \) is the dimension. As is shown in Supplementary Information, upon assuming the potential depends on the square of interparticle distance, the change in energy in unit cell with volume \( v_a \) can be written as

\[
\rho s^\nu = \sum_\xi \frac{\partial \sigma_{\mu\xi}}{\partial R^\nu} = \sum_\nu \sum_\xi C_{\mu\xi\nu\eta} \frac{\partial^2 s^\nu}{\partial R^\nu \partial R^\xi} \tag{8}
\]

To solve this, we try the elastic wave form with an amplitude vector \( e^\nu(q) \):

\[
s^\nu(R, t) = e^\nu(q) e^{i\mathbf{q} \cdot \mathbf{R} - i \omega t} \Rightarrow \rho \omega^2 e^\nu(q) = \sum_\xi \left( \sum_\nu C_{\mu\xi\nu\eta} q^\nu q^\xi \right) e^\nu(q) \tag{9}
\]

B. long-ranged acoustic lattice waves from collective-modes

The review of properties in lattice system and detailed derivation is provided in Supplementary Information. Now we assume particle \( I \) carries mass \( m_I \) and denote \( \Phi^I_l(l) = (\partial^2 U / \partial s^I_l(l) \partial s^J_l(l')) R^J_l(l') \) and the Hessian matrix \( H^\nu_{IJ}(ll') = (\partial^2 U / \partial s^I_l(l) \partial s^J_l(l')) R^J_l(l') \). Here, \( U \) is the total potential energy, directly related to the energy density

\[
\rho s^\nu = \sum_\xi \frac{\partial \sigma_{\mu\xi}}{\partial R^\nu} = \sum_\nu \sum_\xi C_{\mu\xi\nu\eta} \frac{\partial^2 s^\nu}{\partial R^\nu \partial R^\xi} \tag{8}
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\]

B. long-ranged acoustic lattice waves from collective-modes
used before, $\mathbf{U} = \mathbf{U} \cdot \mathbf{V}$ where $\mathbf{V}$ is the volume of the whole system. Physically, $-\Phi^0_i(l)$ is the force on $(l, I)$ in the configuration $R_0$ while $-H^\mu(\mu W)$ is, to the 1st order of accuracy, the $\mu$-component of the force on $(l, I)$ due to the displacement of $(l', J)$ along $\nu$-direction.

It can be shown that upon assuming harmonic approximation, when the position of nucleus changes from $R^\nu(\mu W)$ to $R^{\nu'}(\mu W')$, it obeys the equation of motion:

$$m_l s^{\nu}_l(I) = -\sum_{\nu'J_{\nu'}} H^{\nu}_{\nu'}(\mu W')s^{\nu'}_{\nu'}(I').$$  \hfill (10)

We look for wave solutions that $s^{\nu}_l(I) = e^{\nu}_I e^{\nu \mathbf{R}_{l}^{I}(l)} - i\omega / \sqrt{m_l}$ where $\mathbf{q}$ is an arbitrary vector in the reciprocal space (|q| is wave number). Substituting the ansatz into (10) gives:

$$\omega^2(q, j) e^{\nu}_I(q, j) = \sum_{\nu J} D^{\mu}_{\nu J}(q) e^{\mu}_{\nu J}(q, j), j = 1, 2, ..., N_d.$$

with the dynamical matrix defined as:

$$D^{\mu}_{\nu J}(q) = \frac{1}{(m_{l+} m_{l+})^{1/2}} \sum_{l'} H^{\mu}_{\nu l'}(q) e^{-i q \mathbf{R}_{l'}(l'), l \rightarrow l'}.$$ \hfill (12)

Depending on each $\mathbf{q}$, there exists $N_d$ solutions. It is clear to see the symmetric properties of the dynamical matrix:

$$D^{\mu}_{\nu J}(q) = D^{\nu}_{\mu J}(q) = D^{\nu}_{\mu J}(-q).$$ \hfill (13)

We consider perturbation in the wavevector from $\mathbf{q} = 0$ along one of 1D acoustic branches. For small number $\epsilon$ we have:

$$D^{\mu}_{\nu J}(\epsilon \mathbf{q}) = [D^{\mu}_{\nu J}(0)] + \epsilon \sum_{\xi} [D^{\mu}_{\nu J} \xi(1)] q^{\xi} + \frac{\epsilon^2}{2} \sum_{\xi \xi} [D^{\mu}_{\nu J} \xi(2)] q^{\xi^*} + ...

$$

$$\omega(q, \epsilon \mathbf{q}, j) = \omega^0(q, j) + \epsilon^2 \omega^2(q, j) + ...$$ \hfill (15)

$$e^{\mu}_I(q, j) = [e^{\mu}_I(q, j)](0) + i \epsilon e^{\mu}_I(q, j)(1) + \frac{\epsilon^2}{2} [e^{\mu}_I(q, j)](2) + ...

$$

Note that we use $\epsilon$ to highlight that the perturbation means the expansion of small amplitudes in $\mathbf{q}$. Substituting Eqs. (14)-(15) into Eq. (11) and for each order of $\epsilon$, we have:

$$e^0 : 0 = \sum_{\nu J} [D^{\mu}_{\nu J}(0)[e^{\nu}_I(0, j)]^{(0)}$$ \hfill (17)

$$e^1 : 0 = \sum_{\nu J} [D^{\mu}_{\nu J} \xi(1)] q^{\xi}[e^{\nu}_I(0, j)]^{(0)} + \sum_{\nu J} [D^{\mu}_{\nu J}(0)[e^{\nu}_I(0, j)]^{(1)}$$ \hfill (18)

$$e^2 : \omega^0(q, 1)^2 [e^{\nu}_I(0, j)]^{(0)} + \frac{\epsilon}{2} \sum_{\nu J} [D^{\mu}_{\nu J} \xi \xi(2)] q^{\xi^*} [e^{\nu}_I(0, j)]^{(0)}$$ \hfill (19)

$$- \sum_{\nu J} [D^{\mu}_{\nu J} \xi(1)] q^{\xi} [e^{\nu}_I(0, j)]^{(0)} + \frac{\epsilon}{2} \sum_{\nu J} [D^{\mu}_{\nu J}(0)[e^{\nu}_I(0, j)]^{(2)}$$

The LHS in Eqs. (17,18) are set to zero because the acoustic mode vanishes at zero frequency. For the 0th order, the solution is obvious because of the specific symmetric properties of matrix $D^{\mu}_{\nu J}$, listed in the Eq. (11) in Supplementary Information. We have $[e^{\mu}_I(0, j)]^{(0)} = \sqrt{m_l} u^{\mu}(j)$ for arbitrary $u^{\mu}(j)$. In the linear order result, Eq. (18) can be written as:

$$\sum_{\nu J} [D^{\mu}_{\nu J}(0)[e^{\nu}_I(0, j)]^{(1)} = -\sum_{\nu J_{\xi}} [D^{\mu}_{\nu J} \xi(1)] q^{\xi} [e^{\nu}_I(0, j)]^{(0)}.$$ \hfill (20)

Also using properties (Eq. (11)) in Supplementary Information, we find the equation vanishes by multiplying $\sum_{l} \sqrt{m_l}$ on both sides, which reduces to $(N - 1)$ independent equations for unknown $[e^{\mu}_I(0, j)]^{(0)}$. In this case, the symmetric matrix $[D^{\mu}_{\nu J}(0)]$ is $(N - 1) d \times (N - 1) d$ and its inverse $\Gamma^{\mu}_{\nu J}$ is also symmetric. Without loss of generality, we can let $[e^{\mu}_I(0, j)]^{(0)} = 0$, $\mu = 1, ..., d$ and extend $\Gamma^{\mu}_{\nu J}, I, J \neq 0 \rightarrow N d \times N d$ by letting $\Gamma^{\mu}_{\nu J} = 0$ if $I$ or $J = 0$. Then:

$$[e^{\mu}_I(0, j)]^{(1)} = -\sum_{l \xi} \sum_{J_{\xi}} \gamma^{\mu}_{\nu J} \sum_{J_{\xi}} \sqrt{m_l} [D^{\mu}_{\nu J} \xi(1)] q^{\xi} u^{\nu}(j)$$ \hfill (21)

Given the solutions of 0th and 1st order, we have for the 2nd order Eq. (19) to be written as:

$$\frac{1}{2} \sum_{\nu J} [D^{\mu}_{\nu J}(0)[e^{\nu}_I(0, j)]^{(2)} = \omega^0(q, j)^2 \sqrt{m_l} u^{\mu}(j)$$

$$- \frac{1}{2} \sum_{\nu J_{\xi}} \sqrt{m_l} [D^{\mu}_{\nu J} \xi(2)] q^{\xi^*} u^{\nu}(j)$$

$$- \sum_{l \xi} \gamma^{\mu}_{\nu J} \sum_{J_{\xi}} [D^{\mu}_{\nu J} \xi \xi(1)] q^{\xi} \sqrt{m_l} q^{\xi^*} u^{\nu}(j)$$ \hfill (22)

We can still use the properties of the matrix $D^{\mu}_{\nu J}$ as before, resulting in that after multiplying $\sum_{l} \sqrt{m_l}$ on both sides, the LHS of Eq. (22) vanishes. After this operation, we are left with (divided by the volume of unit cell $v_a$):
\[
\left( \frac{\sum_{i} m_i}{v_a} \right) [\omega(1)(0,j)]^2 u^\mu(j) = \sum_\nu \left\{ \sum_\xi [\mu\nu,\xi_\nu] q^\xi q^\nu + \sum_\xi (\mu\nu,\xi) q^\xi q^\nu \right\} u^\nu(j),
\]

where the matrix coefficients in the RHS are:

\[
[\mu\nu,\xi_\nu] = \frac{1}{2} v_a \sum_{IJ} \sqrt{m_i m_j} [D_{IJ}^{\mu\nu,\xi}]^{(2)} = [\mu\nu,\xi_\nu] = [\mu\nu,\xi_\nu]
\]

\[
(\mu\xi,\nu_\xi) = -\frac{1}{v_a} \sum_{IJ,\alpha,\beta} \Gamma^\alpha_{IJ,\beta} \left( \sum_{K} [D_{IK}^{\alpha\mu,\xi}]^{(1)} \sqrt{m_K} \right) \left( \sum_{L} [D_{JL}^{\beta\nu,\xi}]^{(1)} \sqrt{m_L} \right) = (\xi_\nu,\mu_\nu) = (\nu_\xi,\xi_\mu)
\]

Comparing Eqs. (9) and (23), we finally obtain the relation defining the matrix elements of the elastic coefficients:

\[
\sum_\xi C_{\mu\xi,\nu_\xi} q^\xi q^\nu = \sum_\xi \{[\mu\nu,\xi_\nu] + (\mu\xi,\nu_\nu)\} q^\xi q^\nu \\
\Rightarrow C_{\mu\xi,\nu_\xi} + C_{\mu\nu,\xi_\nu} = 2[\mu\nu,\xi_\nu] + (\mu\xi,\nu_\nu) + (\mu,\xi_\nu) (25)
\]

Eqs. (25) connects the dynamical matrix and the elastic constants. In case the lattice has a centre of symmetry, two terms labeled as \((\cdot,\cdot)\) vanish.

### C. the LM formalism

Nonaffine lattice dynamics has been studied systematically in the LM formalism, which is applicable to either amorphous materials or crystals. In its framework, the response to external strain is called affine if the inter-particle displacements are just the old positions transformed by the macroscopic strain tensor. In a disordered, or a non-centrosymmetric lattice where local inversion symmetry is absent, the situation becomes different since forces from surrounding environment acting on every particle no longer cancel by symmetry. However, they have to be relaxed with additional particle displacements such that the whole system remains in mechanical equilibrium at every step in the deformation, as shown in [12], and these additional atomic displacements are called nonaffine displacements.

In language of elasticity, particles are assumed to lie in a unit cell described by three Bravais vectors \(h = (a, b, c)\). Thus, the interaction potential depends on both \(R^I_j\) and \(R^I_j\), \(U = U(R^I_j, h)\) and any vector \(R\) is mapped onto a cubic reference cell: \(R = h w, w^\nu \in [-0.5, 0.5]\). We use the unit cell as it prior to deformation as the reference frame \(h\) and denote the deformed cell by \(h\).

When the tagged particle undergoes a displacement to the position \(R^I_j\), the process can be understood to consist of two steps: initially, we have \(R^I_j = F R^I_j\) where \(F = h^{-1}h\) is the deformation gradient tensor. \(F\) describes an affine transformation of the unit cell whereas \(\hat{R}^I_j\) remains unchanged. I further introduce the Cauchy-Green strain tensor \(\eta = (R^I_j F - I) / 2\) to describe the deformations, as described in [13][13]. In the linear regime of elasticity, the tensor \(\eta_{\mu\nu}\) is the same as the classical strain tensor, as defined in Eq. (4). The potential energy can be written either in the reference frame, or in the deformed frame, \(U((R^I_j), \eta) \equiv U((R^I_j), \eta)\). Thus, in the reference frame \(\{R^I_j\}\), changing \(\eta\) means the response to affine strain of the whole system: the following change in the reference configuration \(\{\hat{R}^I_j\}\) corresponds to additional nonaffine displacements. In other words, in the second step of the process, particles perform non-affine displacements by relaxing to their nearest equilibrium position \(\{\hat{R}^I_j\}\), while the shape of cell, \(h\) (and hence \(F\)), remains unchanged. Those new coordinates are generally different from the affine positions derived by the reference coordinates, \(\{R^I_j\} \neq \{\hat{R}^I_j\}\).

When the linear strain is applied slow enough, the deformation can be regarded as static and mechanical equilibrium is valid at any stage. I can expand the force acting on an individual particle \(I, f^I_\nu = -\partial U / \partial R^I_j\), in terms of the components of the strain tensor \(\eta\) and \(\{R^I_j\}\), as down in [10][10]:

\[
\delta f^I_\nu = \sum_{J\nu} \frac{\partial^2 U}{\partial R^J_j \partial \eta^I_\xi} \delta R^J_j + \frac{\partial^2 U}{\partial R^I_j \partial \eta^I_\xi} \delta \eta^I_\xi = 0.
\]

This is equivalent to the \(Nd\) linear system of equations for the nonaffine displacements \(\delta R^I_j\):

\[
\sum_{J\nu} H^I_\nu J \delta R^J_I = -\Xi^I_\nu \delta \eta^I_\xi, \quad (27)
\]

where the Hessian matrix \(H^I_\nu J\) and the affine force field \(\Xi^I_\nu \delta \eta^I_\xi\) are defined as:

\[
H^I_\nu J = \frac{\partial^2 U}{\partial R^I_j \partial R^J_j}, \quad \Xi^I_\nu \delta \eta^I_\xi = -\frac{\partial^2 U}{\partial R^I_j \partial \eta^I_\xi}.
\]
Assuming pairwise interaction, it is easy to see the Hessian matrix is real and symmetric. Hence, it can be diagonalised as $H = PA\lambda P^T$ where $\Lambda$ is the diagonal matrix consisting of eigenvalues of $H$, and $P$ is the orthogonal matrix with $(PP^T = P^TP = I)$ whose columns are made of corresponding normalised eigenvectors. Denoting $\delta \tilde{R} = P^T \delta \tilde{R}$, I have, from transforming Eq. (27)

$$ \Lambda \delta \tilde{R} = -P^T \tilde{\Xi} \delta \eta_{\xi i}. $$

(29)

Here, vectors originally written in $d$-dimensional space transformed to $Nd$-vectors labeled by an arrow above the symbol. Because of translation invariance, the Hessian matrix contains $d$ zero eigenvalues, so $\Lambda = \text{diag}\{0,0,\ldots,\lambda_{d+1},\ldots,\lambda_{Nd}\}$ where I assume the ordering in eigenvalues without loss of generality. This means, only $\delta \tilde{R}_j, j = d+1,\ldots, Nd$ can be solved:

$$
\begin{pmatrix}
\delta \tilde{R}_{d+1} \\
\vdots \\
\delta \tilde{R}_{Nd}
\end{pmatrix} = -
\begin{pmatrix}
\lambda_{d+1} \tilde{\xi}_{d+1} \\
\vdots \\
\lambda_{Nd} \tilde{\xi}_{Nd}
\end{pmatrix}
\begin{pmatrix}
e_{d+1} \\
\vdots \\
e_{Nd}
\end{pmatrix}
\begin{pmatrix}
\delta \tilde{\xi}_{d+1} \\
\vdots \\
\delta \tilde{\xi}_{Nd}
\end{pmatrix}
$$

(30)

where $\tilde{e}_j, j = 1,\ldots, Nd$ are orthonormal eigenvectors of the Hessian matrix. Transferring back to $\delta R_j, j = 1,\ldots, Nd$, I obtain

$$
\frac{\delta R_j}{\delta \eta_{\xi i}} = -\sum_{i=1}^{d} e_{ij} \delta \tilde{R}_i - \sum_{i=d+1}^{Nd} e_{ij} \left( \frac{\tilde{e}_i \cdot \tilde{\xi}_{\xi i}}{\lambda_i} \right).
$$

(31)

Here, $e_{ij}$ is the $(i, j)$ element of $P$ and $\delta \tilde{R}_i, i = 1,\ldots, d$ are unknown. The elastic constant is defined as the second derivative of potential energy $U$ with respect to the strain tensor per unit volume: $C_{\mu \nu \xi i} = (\partial^2 U/\partial \eta_{\mu \nu} \partial \eta_{\xi i})/V$. The material derivative is denoted as $D$. Because of mechanical equilibrium, it is easy to verify $D\tilde{U}/D\eta = \partial \tilde{U}/\partial \eta$. Then the elastic modulus is calculated as

$$
C_{\mu \nu \xi i} = \frac{1}{V} \frac{\partial^2 U}{D \eta_{\mu \nu} D \eta_{\xi i}}
= \frac{1}{V} \left( \frac{\partial^2 U}{\partial \eta_{\mu \nu} \partial \eta_{\xi i}} + \sum_{1 \leq k \leq d} \frac{\partial^2 U}{\partial \eta_{\mu \nu} \partial \eta_{\xi i}} \cdot \frac{D \tilde{R}_k}{D \eta_{\xi i}} \right)
= \frac{1}{V} \frac{\partial^2 U}{\partial \eta_{\mu \nu} \partial \eta_{\xi i}} + \frac{1}{V} \sum_{1 \leq k \leq d} \tilde{\xi}_{\mu \nu}^{k, \xi i} \frac{D \tilde{R}_k}{D \eta_{\xi i}}
\equiv C_{\mu \nu \xi i}^A + C_{\mu \nu \xi i}^{NA}.
$$

(32)

Using Eq. (31), we write the nonaffine elasticity, $C_{\mu \nu \xi i}^{NA}$, as

$$
C_{\mu \nu \xi i}^{NA} = \frac{1}{V} \sum_{j=1}^{Nd} \tilde{\xi}_{\mu \nu}^{j, \xi i} \frac{\delta \tilde{R}_j}{\delta \eta_{\xi i}}
= \frac{1}{V} \sum_{j=1}^{Nd} \tilde{\xi}_{\mu \nu}^{j, \xi i} \left( -\sum_{i=1}^{d} e_{ij} \delta \tilde{R}_i - \sum_{i=d+1}^{Nd} e_{ij} \left( \frac{\tilde{e}_i \cdot \tilde{\xi}_{\xi i}}{\lambda_i} \right) \right)
= -\frac{1}{V} \sum_{i=1}^{d} \left( \tilde{e}_i \cdot \tilde{\xi}_{\mu \nu} \right) \left( \frac{\delta \tilde{R}_i}{\lambda_i} \right) - \frac{1}{V} \sum_{i=d+1}^{Nd} \left( \tilde{e}_i \cdot \tilde{\xi}_{\mu \nu} \right) \left( \frac{\delta \tilde{R}_i}{\lambda_i} \right)
$$

(33)

As for the inner product in the 1st term on the RHS, since the eigenvector $\tilde{e}_i, i = 1,\ldots, d$ corresponds to zero eigenvalue, they have the form $e_{ij} = 1/\sqrt{N}$ if $j$ is a multiply of $i$ and $e_{ij} = 0$ otherwise, for $j = 1,\ldots, Nd$. Therefore, $\tilde{e}_i \cdot \tilde{\xi}_{\mu \nu} \propto \sum_i \tilde{\xi}_{\mu \nu}^{i, \xi i}$. In this paper, we only consider pairwise interaction in harmonic approximation, so from Eq. (28) the affine force field $\tilde{\xi}_{\mu \nu}^{i, \xi i}$ can be expressed as follows:

$$
\tilde{\xi}_{\mu \nu}^{i, \xi i} = -\sum_j \frac{\partial^2 U}{\partial \tilde{R}_j^\mu \partial \tilde{R}_j^\nu} \frac{\partial \tilde{R}_j^\mu}{\partial \eta_{\xi i}}
\begin{pmatrix}
\delta \tilde{R}_j^\mu \\
\delta \tilde{R}_j^\nu
\end{pmatrix} = \sum_j \left[ (\tilde{R}_{j1} s_{j1} - t_{j1}) n_{j1}^\mu n_{j1}^\nu + \frac{1}{2} t_{j1}(\delta_{\mu \nu} n_{j1}^\mu + \delta_{\nu \mu} n_{j1}^\nu) \right]
= \sum_j (\tilde{R}_{j1} s_{j1} - t_{j1}) n_{j1}^\mu n_{j1}^\nu,
$$

(34)

with the orientation unit vector $n^\mu$, tension of a bond $t_{j1}$, and stiffness of the bond $s_{j1}$ defined as

$$
\tilde{R}_{j1} = \tilde{R}_{j1}^\mu, \quad t_{j1} = \frac{\partial U}{\partial \tilde{R}_j^\mu}, \quad s_{j1} = \frac{\partial^2 U}{\partial \tilde{R}_j^\mu \partial \tilde{R}_j^\nu}.
$$

(35)

Here, by $\tilde{R}_{j1}^\mu$, we mean $\tilde{R}_{j1}^\mu = \tilde{R}_{j1}^\mu - \tilde{R}_{j1}^\nu$. To get the 2nd equality in Eq. (34), we used the identity $\partial \tilde{R}_j^\mu / \partial \eta_{\xi i} = (\delta_{\mu \nu} \tilde{R}_j^\mu + \delta_{\nu \mu} \tilde{R}_j^\nu)$. The 2nd term in square bracket vanishes because of the mechanical equilibrium condition. Now it is clear that the first term in Eq. (33) vanishes due to the inversion symmetry of $n_{j1}$, i.e. $n_{j1} = -n_{j1}$. Thus, the remaining (negative) nonaffine elastic constant can be written as

$$
C_{\mu \nu \xi i}^{NA} = \frac{1}{V} \sum_{i=d+1}^{Nd} \left( \tilde{e}_i \cdot \tilde{\xi}_{\mu \nu} \right) \left( \frac{\delta \tilde{R}_i}{\lambda_i} \right) < 0
$$

(36)

where contributions from zero eigenvalues are excluded in the summation.

### III. NONAFFINE ELASTICITY

We note that, in the BH method (see Eq. (5)) objects like

$$
\{ \mu \nu \xi i \}; \begin{pmatrix} I & J \end{pmatrix}; \begin{pmatrix} I & \nu \xi \end{pmatrix}
$$
are mathematically equivalent to affine elastic constant \( C_{\mu\nu\xi\zeta} \), the Hessian matrix \( H_{I,J}^{\mu\nu} \) and affine force field \( \Xi_{I,\xi}^{\mu\nu} \). Therefore, when we take a derivative of Eq. (6) with respect to the strain \( \eta_{\mu\nu} \), we do recover Eq. (27). Since the Hessian always has \( d \) zero eigenvalues and is non-invertible. Rather than taking normal mode decomposing and simply ignore zero eigenmodes, one should instead introduce reduced \( \tilde{H}_{I,J}^{\mu\nu} \) and \( \tilde{\Xi}_{I,\xi}^{\mu\nu} \) by deleting, say the first \( d \) rows and columns in \( H_{I,J}^{\mu\nu} \) and first \( d \) elements in \( \Xi_{I,\xi}^{\mu\nu} \), respectively. The reduced \( \tilde{H}_{I,J}^{\mu\nu} \) is symmetric and invertible (see details in Supplementary Information).

Thus, the energy density becomes

\[
U = \frac{1}{2} \sum_{I,J,\mu\nu} \tilde{H}_{I,J}^{\mu\nu} s_I^{\mu\nu} s_J^{\mu\nu} + \sum_{I,\mu\nu\zeta} \tilde{\Xi}_{I,\zeta}^{\mu\nu\zeta} \eta_{I,\zeta} + \frac{1}{2} C_{\mu\nu\xi\zeta} \eta_{I,\xi} \eta_{I,\xi}
\]

which takes minimum when

\[
0 = \sum_{J,\nu} \tilde{H}_{I,J}^{\mu\nu} s_J^{\nu} + \sum_{\zeta} \tilde{\Xi}_{I,\zeta}^{\nu\zeta} \eta_{I,\zeta}.
\]

Solving the minimization condition for nonaffine displacements \( s_J^{\nu} \), and substituting back to Eq. (37), gives the nonaffine correction to affine elastic constant

\[
C_{\mu\nu\xi\zeta} = C_{\mu\nu\xi\zeta}^{A} - C_{\mu\nu\xi\zeta}^{NA}
\]

\[
= \frac{1}{V} \frac{\partial^2 U}{\partial \eta_{\mu\nu} \partial \eta_{\xi\zeta}} - \frac{1}{V} \sum_{I,J,K} \tilde{\Xi}_{I,\xi\zeta}^{\mu\nu\zeta} (\tilde{H}_{I,K}^{\mu\nu} )^{-1} \tilde{\Xi}_{K,\xi\zeta}^{\mu\nu\zeta} \quad (39)
\]

Compare \( C^{NA} \) in Eq. (39) with the nonaffine correction in LM's method, Eq. (36), we remark these two objects will surprisingly produce the same results, although they have different mathematical expressions. We name the way to get elastic constants via the reduced Hessian matrix and reduced affine force field as “the method of reduced fields”.

In the following parts, we test all methods in previous sections for some mechanical models. First of all, consider the simplest elastic system, the 1D linear chains of equal masses \( M \) connected by springs \( k \), as shown in Fig. (1b). In this case, the potential energy of a deformed string is \( U = \sum_n \left( R(n+1) - R(n) \right)^2 (1 + \eta)^2 k/2 \) with the Hessian matrix being simply a number: \( H = 2k \). If we want to preserve the lattice periodicity in the disordered state, then there cannot have nonaffine deformations. The elastic modulus, in all three methods, is \( C = ak \).

**A. 1D linear chain with two masses in a cell**

We consider 1D linear chain with two masses connected via springs with the same spring constant \( k \) but different original lengths (see Fig. (1b)). The size of each cell is \( a \), within which the original length of spring between masses \( M \) and \( m \) is \( x \) and \( y = a - x \) is the original length of the spring across the cell. We firstly refer to the BH method

\[
\begin{align*}
M \ddot{s}_1(n) &= -2k \left[ s_1(n) - \frac{s_2(n) + s_2(n - 1)}{2} \right] \\
M \ddot{s}_2(n) &= -2k \left[ s_2(n) - \frac{s_1(n) + s_1(n + 1)}{2} \right].
\end{align*}
\]

To make it convenient for calculation, we let \( M = m \) and use Eq. (25). The elastic constant can be calculated and

![Diagram](image-url)
gives the same form (see in Supplementary Information),

\[ C = \frac{ak}{2}. \]

To test the LM formalism in Section II.C, we write potential energy as

\[ U = \sum \alpha V_\alpha = k \sum \alpha [(R_2(n) - R_1(n) - x)^2 + (R_1(n+1) - R_2(n) - y)^2]/2. \]

After putting the strain \( \eta \),

\[
V_\alpha(\eta) = \frac{k}{2}(1 + \eta)(R_2(n) - R_1(n)) - x^2 + \frac{k}{2}(1 + \eta)(R_1(n+1) - R_2(n)) - y^2 \quad (44)
\]

and

\[
C^A = \frac{1}{a} \frac{\partial^2 V_\alpha(\eta)}{\partial \eta^2} = \frac{k}{a}(x^2 + y^2)
\]

\[
F_{R_1(n)}(\eta) = -\frac{\partial V_\alpha(\eta)}{\partial R_1(n)} = k[(1 + \eta)(R_2(n) - R_1(n)) - x] - k[(1 + \eta)(R_1(n) - R_2(n)) - y] \]

\[ \Xi_{R_1(n)} = \frac{\partial}{\partial \eta} F_{R_1(n)}(\eta) = k(x - y) \quad (45) \]

And similarly,

\[
F_{R_2(n)} = k[(1 + \eta)(R_2(n) - R_1(n) - x)] + k[(1 + \eta)(R_1(n+1) - R_2(n) - y)]
\]

\[
\Xi_{R_2(n)} = k(y - x) \quad (46) \]

Initial equilibrium condition requires \( F_{R_1(\alpha)}(0) \) and \( F_{R_2(\alpha)}(0) \) are zero, so \( R_2(n) - R_1(n) = x, R_1(n) - R_2(n - 1) = y \). The Hessian matrix is

\[
H = k \begin{pmatrix} 2 & -2 \\ -2 & 2 \end{pmatrix}, \quad (47)
\]

whose eigenvalues are \( \lambda_1 = 0, \lambda_2 = 4k \), with the eigenvectors corresponding to \( \xi_1 = 1/\sqrt{2}(1, 1), \xi_2 = 1/\sqrt{2}(1, -1) \). From Eq. (32), we have

\[ C = C^A - \frac{1}{a} \frac{(\Xi \cdot \xi_2)^2}{\lambda_2} = \frac{ak}{2} \quad (48) \]

which is consistent with the BH results.

Last, we check if the reduced Hessian and affine force field, as discussed in Eq. (39), can reproduce the correct elastic constant. Deleting the first row and column in \( H \) and the first element in \( \Xi \), we obtain \( H = 2k \Xi \Xi \).

\[
C = C^A = \frac{(k/\alpha)(x^2 + y^2)}{2a},
\]

this again gives the correct elastic constant: \( C = ak/2 \).

**B. Nonaffinity in non-centrosymmetric lattices**

To gain a deeper insight into the original LM formalism and the reduced field method proposed in the paper, we choose a typical non-centrosymmetric lattice system, \( \alpha \)-quartz, as studied in [9]. The conventional unit cell, as shown in Fig. 2 contains three molecules of \( \text{SiO}_2 \). The empirical potential is composed of a short-range Buckingham potential plus long-range Coulombic interactions between Si and O atoms [17–19]. In particular, the short-range potential between atoms \( I \) and \( J \) is:

\[
\Phi_{I,J}^{\text{sh}}(R_{IJ}) = \left\{ A_{IJ}e^{-\frac{R_{IJ}}{\sigma_{IJ}}} - C_{IJ} - \left[ A_{IJ}e^{-\frac{q_{I,sh}}{\sigma_{IJ}}} - C_{IJ} \right] \right\} \times \Theta(R_{c,sh} - R_{IJ}), \quad (50)
\]

where \( \Theta(R) \) is the Heaviside step function. The cut-off distance is set to be \( R_{c,sh} = 10\text{Å} \) to obtain the best agreement with experimental data [19]. For the Coulombic part, the classical Ewald method was used [11, 20–22], with the total electrostatic energy then made of three contributions: short-range term in real space, a long-range term in Fourier space and a self-interaction constant:

\[
E = E_{SR} + E_{LR} + E_{SI}
\]

\[
= \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{I \neq J} \frac{q_Iq_J}{R_{IJ}} \text{erfc}(\frac{R_{IJ}}{\sqrt{2}\sigma}) - \frac{1}{2V_\epsilon} \sum_{G \neq 0} \frac{\exp(-\sigma^2G^2/2)}{G^2} |S(G)|^2
\]

\[
- \frac{1}{4\pi\epsilon_0} \frac{1}{2\sqrt{\pi}\sigma} \sum_{I} q_I^2, \quad (51)
\]

where \( q_I \) is the charge on atom \( I \), \( \text{erfc}(x) = 1 - 2/\sqrt{\pi} \int_0^x \exp(t^2)dt \) is the complementary error function, reciprocal lattice vectors are represented by \( G = 2\pi[n_x/L_x,n_y/L_y,n_z/L_z] \), and \( S(G) = \sum_{I} q_I \exp(iG \cdot \)
（R_f）is the structure factor. The dimensions of the simulation cell are labeled as L_x, L_y, L_z, which are assumed periodic and orthogonal. The parameter σ is the standard deviation of the Gaussian distribution. In the literature, one may also find the use of parameter α = 1/√2σ. The cut-off radius for the real space potential is R_{cut} = 3.12/α = 10Å and a summation in reciprocal space goes up to n_{μ,max} = αL_μ. Note that, among these potential energies, the Si-Si longer-range interaction is ignored, because the remaining parts already provide the best agreement with experimental measurements of elastic constants of α-quartz [19]. The simulation in [9] uses a finite system with 1350 atoms in a periodic orthogonal cell. The structure is relaxed at 0K by energy minimization, followed by adapting the cell dimensions with a barostat to impose zero internal stress, with equilibrium lattice constants obtained. Table I lists some elastic moduli calculated from the LM formalism, Eq. (32) and from the method of reduced fields in Section III, Eq. (39). It is clear that, the results are exactly the same between two methods.

### IV. CONCLUSION

In conclusion, having reviewed several approaches to linear elastic constants, we find that in the BH framework, nonaffine elasticity is essentially due to the local additional (Helmholtz) displacements particles experience. In contrast, in the LM formalism, the affine fields of local (Gibbs) forces arising from the break of inversion symmetry are instead the cause of nonaffinity. The two methods are equivalent, in the sense that the change of potential energy under the linear strain is minimized, or the mechanical equilibrium condition holds. We also emphasise that, the direct normal mode decomposition to the Hessian matrix always contains zero modes. Taking account to non-zero modes only would lead to the correct nonaffine elasticity, which is the same as the result from the reduced method of reduced fields. We thus point out that, the scaling of nonaffine elasticity in [10] [23] should be adjusted correspondingly. Our studies here focus on the periodic lattice, but there is no difficulty for such an analysis to be applied in disordered materials.

Moreover, only static (equilibrium) elasticity is considered in this paper. It would be of interest to check how these methods are applied for visco-elastic responses.

### ACKNOWLEDGMENTS

B. C acknowledges the financial support of CSC-Cambridge Scholarship. Discussions with A. Zaccone are gratefully acknowledged.

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