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Abstract
We derive expressions for the shear modulus of deeply quenched, glassy solids, in terms of a
Cauchy–Born free energy expansion around a rigid (quenched) reference state, following the
approach due to Alexander (1998 *Phys. Rep.* **296** 65). Continuum-limit explicit expressions of
the shear modulus are derived starting from the microscopic Hamiltonians of central and
bond-bending interactions. The applicability of the expressions to dense covalent glasses as
well as colloidal glasses involving strongly attractive or adhesive bonds is discussed.

1. Introduction

While the structure, elasticity and lattice dynamics of condensed matter with long-range order (thanks to the intrinsic symmetry of crystalline structures) are fairly well understood [1], the same cannot be said of amorphous solids. Recent advances include the unveiling of connections between disordered solids made of thermal particles (glasses) and granular packings, so that the puzzling properties found in both these classes of materials can be investigated by means of unifying concepts. Well-known examples are the excess of low-frequency modes (the so-called boson peak in the vibrational spectrum) [2] and the inhomogeneity of the elastic response [2–4]: features that have been observed in atomic (and molecular) glasses as well as in granular systems. These phenomena, as recent theoretical studies have proposed, may find their origin in the weak connectivity of amorphous solids [5] as well as in their lack of symmetry [4, 6]. Regarding the former aspect, recently it became clear that coordination plays a fundamental role in determining the mechanical properties of marginally rigid solids when only central forces are at play. On the other hand, in the case of strongly connected structures or other dense systems where the bonds between building blocks can support bending moments, nonaffinity is often a very small correction to the affine part; thus the affine approximation works relatively well [7, 8]. Some technologically important systems seem to belong to this class, e.g. dense networks of semi-flexible polymers, strong

attractive colloidal glasses and covalent glasses (e.g. silicon glass) [7, 9].

In the present work, we derive explicit expressions for the macroscopic shear modulus of deeply quenched, arrested states of like particles, using Alexander's Cauchy–Born approach. The validity and application of the results are discussed.

2. Continuum theory of shear elasticity in solids with quenched disorder

In [6], Alexander formulated the systematic Cauchy–Born approach for amorphous solids, based on which the Helmholtz free energy at $T = 0$ (thus coinciding with the internal energy) can be expanded around a *rigid*, stressed, reference configuration where the set of particle positions is denoted by $\{R\}$. In such a low-temperature reference state, as a result of quenching (solidification), particles are *labelled*, in the sense that they occupy well-defined and fixed positions on a (disordered) lattice, the set of which represents just one out of $N!$ possible permutations (N being the total number of particles). In other words, permutation symmetry (which is active in the liquid precursor) is broken in the quenching process [6]. Because of this, as opposed to equilibrium fluids, the disorder average for amorphous solids is of nontrivial definition. To avoid this problem, in Alexander's version of Cauchy–Born theory, the expansion (along with the disorder average) is carried out in terms of the *relative deviations* between particles. As shown in [6], this leads

to the continuum limit and provides the only systematic application of Cauchy–Born theory to disordered solids. In the following we apply this approach to a generic dynamically arrested (glassy) state composed of spherical particles mutually interacting via two-body central and three-body angular (bond-bending) interactions. This may be a suitable model of well-bonded glassy systems such as atomic (covalent or metallic) glasses or attractive colloidal glasses.

Retaining terms up to second order, and including a three-body angular interaction term, the expansion is

$$\delta F \equiv F(\{r\}) - F(\{R\}) \simeq \sum_{\langle ij \rangle} \frac{\partial F}{\partial r_{ij}}\bigg|_{\{R\}} \delta r_{ij}$$
$$+ \frac{1}{2} \sum_{\langle ij \rangle} \frac{\partial^2 F}{\partial r_{ij}^2}\bigg|_{\{R\}} (\delta r_{ij})^2 + \frac{1}{2} \sum_{\langle ijk \rangle} \frac{\partial^2 F}{\partial \Theta_{ijk}^2}\bigg|_{\{R\}} (\delta \Theta_{ijk})^2.$$
$$(2.1)$$

In the first two terms on the rhs, the summation runs over all N_c pairs of pair-interacting particles (i.e. over all bonds) and the derivatives are evaluated at the equilibrium distance in the reference rigid state $R_{ij} \equiv |\mathbf{R}_{ij}|$. In the last term (i.e. the angular interaction or bond-bending term) the summation is over pairs of bonds $[ij]$ and $[ik]$, $i \neq j \neq k$, having one common vertex. In our analysis, we will consider the two-body (central) terms and the three-body (bond-bending) terms in equation (2.1) separately, starting from the former case.

Expanding in the *relative* distance deviations allows one to define a microscopic displacement field $\mathbf{u}_{ij}$:

$$\delta r_{ij} = u_{ij}^{\parallel} + [(u_{ij}^{\perp})^2 / 2 R_{ij}] + \mathcal{O}(r_{ij}^3) \qquad (2.2)$$

which has a component in the direction of $\mathbf{R}_{ij}$, i.e. $u_{ij}^{\parallel} \equiv (\delta \mathbf{R}_i - \delta \mathbf{R}_j) \cdot \hat{\mathbf{R}}_{ij}$, and an orthogonal component, i.e. $u_{ij}^{\perp} \equiv (\delta \mathbf{R}_i - \delta \mathbf{R}_j)^{\perp}$. In the absence of external forces, substituting equation (2.2) into the central interaction terms in equation (2.1), gives

$$\delta F^{(C)} \simeq \sum_{\langle ij \rangle} \frac{\partial F}{\partial r_{ij}}\bigg|_{\{R\}} \frac{[(\delta \mathbf{R}_i - \delta \mathbf{R}_j)^{\perp}]^2}{2 R_{ij}}$$
$$+ \frac{1}{2} \sum_{\langle ij \rangle} \frac{\partial^2 F}{\partial r_{ij}^2}\bigg|_{\{R\}} [(\delta \mathbf{R}_i - \delta \mathbf{R}_j) \cdot \hat{\mathbf{R}}_{ij}]^2. \qquad (2.3)$$

The first-derivative terms correspond to the bond-tension or stress terms associated with the *initial* or quenched stresses (which are, generally, dependent upon the ageing history). These make an important contribution to the rigidity of weakly connected (undercoordinated) materials and actually ensure the existence of a rigid reference state around which one can expand [6]. For central interactions, the second derivative can be written as the bond stiffness $\kappa_{\parallel} \equiv \partial^2 F / \partial r_{ij}^2|_{\{R\}}$, also known as the Born–Huang term. In the case of a glass, these terms are to be evaluated in the stressed state and, in general, may differ from the corresponding terms in crystals at true (thermodynamic) equilibrium (which are evaluated exactly at the position of the minimum of the pair potential). Since, however, the interparticle distances in the stressed state are generally not *a priori* known, a useful and widely used approximation is to evaluate the second derivative of the pair

potential at the distance corresponding to the minimum of the potential well, just as for crystals. Though this approximation is usually not justified for amorphous solids, in the case of deep, short-ranged attractive potential wells, the probability of finding the particle is by far the highest near the minimum of the well. As a consequence, the latter is expected to be a good estimate of the average interparticle distance in these systems also in the stressed state, as shown in [11]. Further, since 'initial stresses in glasses must be internal stresses with a zero average' so that 'the internal stresses cannot contribute to the overall macroscopic shear rigidity', it follows that 'the macroscopic elastic moduli which one measures must be proper Born–Huang shear moduli' [6], as confirmed also within simulation studies [10]. Therefore, the stress terms in the expansion, equation (2.3), can be neglected to a good approximation [6, 10], and one can write

$$\delta F^{(C)} \simeq \frac{1}{2} \kappa_{\parallel} \sum_{\langle ij \rangle} \overline{[(\delta \mathbf{R}_i - \delta \mathbf{R}_j) \cdot \hat{\mathbf{R}}_{ij}]^2} = \frac{1}{2} \kappa_{\parallel} \sum_{\langle ij \rangle} \overline{(u_{ij}^{\parallel})^2}$$
$$(2.4)$$

where $\bar{\cdot}$ denotes the average over all possible *deviations* (i.e. strain configurations) from the reference state. Introducing a smooth (continuous) displacement field $\mathbf{u}(\mathbf{r})$, to lowest order in the gradient expansion one has

$$\overline{u_{ij}^{\parallel}} \simeq (\mathbf{R}_{ij} \cdot \nabla) \mathbf{u}(\mathbf{r}) \cdot \hat{\mathbf{R}}_{ij} = R_{ij}^{-1} R_{ij}^{\alpha} R_{ij}^{\beta} \partial_{\alpha} u_{\beta}, \qquad (2.5)$$

where summation over repeated indices is understood and transposition symmetry is evident. Using this and introducing the affine transformation $\overline{(u_{ij}^{\parallel})^2} \simeq \text{Tr}[(\mathbf{R}_{ij} \otimes \mathbf{R}_{ij}) \cdot \mathbf{e} / R_{ij}]^2$ defined by the disorder-averaged linearized symmetric strain tensor $\mathbf{e} \equiv e_{\alpha\beta} = \frac{1}{2}(\partial_{\alpha} u_{\beta} + \partial_{\beta} u_{\alpha})$, with $\overline{u_{ij}^{\parallel}}^2 - \overline{u_{ij}^{\parallel}}^2 \ll \overline{u_{ij}^{\parallel}}^2$, we obtain the continuum limit [6]:

$$\delta F^{(C)} \simeq \frac{1}{2} \sum_{\langle ij \rangle} \kappa_{\parallel} \overline{(u_{ij}^{\parallel})^2} \simeq \frac{1}{2} \sum_{\langle ij \rangle} \kappa_{\parallel} \left\{ \frac{\text{Tr}[(\mathbf{R}_{ij} \otimes \mathbf{R}_{ij}) \cdot \mathbf{e}]}{R_{ij}} \right\}^2$$
$$(2.6)$$

where $\otimes$ denotes the dyadic product. It is easy to find that for an imposed pure shear deformation the above expression reduces to

$$\delta F^{(C)} \simeq \frac{1}{2} \kappa_{\parallel} \sum_{\langle ij \rangle} 4 R_{ij}^2 \left(\frac{R_{ij}^x}{R_{ij}} \frac{R_{ij}^y}{R_{ij}} \right)^2 e_{xy}^2. \qquad (2.7)$$

For the quenched configuration $\{R\}$, under the assumption that pair (two-body) interactions are much stronger than higher-order multi-body interactions, the summation over pairs of nearest neighbours can be replaced by the total number of bonds, N_c. This implies an average over all possible spatial orientations of the bonds in the reference state $\{R\}$:

$$\delta F^{(C)} \simeq \frac{1}{2} \kappa_{\parallel} N_c \langle 4 R_{ij}^2 (\hat{R}_{ij}^x \hat{R}_{ij}^y)^2 e_{xy}^2 \rangle_{\Omega}$$
$$\simeq 2 \kappa_{\parallel} N_c R_0^2 \langle (\hat{R}_{ij}^x \hat{R}_{ij}^y)^2 \rangle_{\Omega} e_{xy}^2 \qquad (2.8)$$

where $R_{ij} \equiv R_0$ is the average interparticle distance in the reference quenched configuration and $\langle \cdot \rangle_{\Omega}$ denotes the angular average. Introducing the mean coordination z, and noting that

$N_c/V \equiv \frac{1}{2}zN/V \equiv 3z\phi/\pi R_0^d$, leads to the following form for the free energy density:

$$\delta\tilde{F}^{(C)} \simeq 6\pi^{-1}\kappa_\| z\phi R_0^{2-d}\langle(\hat{R}_{ij}^x\hat{R}_{ij}^y)^2\rangle_\Omega e_{xy}^2. \qquad (2.9)$$

where d is the dimensionality of space. For $d = 3$, using spherical coordinates $\hat{\mathbf{R}}_{ij} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, 1)$, with $R_{ij}^x = \sin\theta\cos\varphi$, $R_{ij}^y = \sin\theta\sin\varphi$ and assuming that the particles have zero degree of spatial correlation, averaging gives

$$\langle(\hat{R}_{ij}^x\hat{R}_{ij}^y)^2\rangle_\Omega = \frac{1}{4\pi}\int\int d\varphi\,\sin\theta\,d\theta(\sin^4\theta\cos^2\varphi\sin^2\varphi)$$
$$= \frac{1}{15}. \qquad (2.10)$$

At $T = 0$, $\sigma_{\alpha\beta} \equiv \partial\delta F/\partial e_{\alpha\beta}$ and the affine translation–rotation invariant shear modulus for the central-force case can be derived as

$$G^{(C)} \simeq \frac{4}{5\pi}\kappa_\| z\phi R_0^{-1}. \qquad (2.11)$$

Note that this expression has been derived using the definition of linearized strain tensor. In experiments and simulations the engineering strain tensor defined as $\gamma_{xy} \equiv 2e_{xy}$ is often used. This leads to a prefactor $2/5\pi$ in equation (2.11) instead of $4/5\pi$ whenever equation (2.11) is to be compared with experimental measurements of G where the stress is measured as a function of the engineering strain (e.g. in [11]).

The coordination number z can be estimated from the experimentally determined structure factor, or evaluated, for sufficiently dense glasses, according to the following route. If the glass is dense ($\phi > 0.5$) its structure is homogeneous due to mutual impenetrability of the particles and therefore dominated by the hard-sphere component of interaction. As shown by recent experimental studies [12], the result is that dense ($\phi \sim 0.6$) strongly attractive glasses exhibit the same homogeneous structure of purely hard-sphere glasses. Therefore, it is possible to estimate the mean coordination as a function of the packing fraction ϕ, by calculating the mean coordination of the *hyper-quenched* hard-sphere liquid with the same ϕ. This is equivalent to integrating the radial distribution function of hard-sphere liquids with a cutoff on the integration determined so as to recover the jamming point of monodisperse hard spheres (given as $z = 6$ at $\phi \simeq 0.64$). This route has been used to interpret experimental data of attractive colloidal glasses in [11].

Equation (2.11) has been obtained under the limiting assumption that, in very attractive systems, the affine approximation leads to a small error. However, in spite of that approximation, in [11] it has been shown that equation (2.11) gives a rather accurate quantitative description of the shear modulus of short-ranged attractive (depletion) colloidal glasses such as those studied in [13]. In that case, the affine approximation is justified because the elastic response is dominated by the first linear regime ending with the break up of nearest-neighbour bonds [13].

The more general expansion in equation (2.1) involves the three-body bond-bending forces and is somewhat more complex. A suitable model, which satisfies translation–rotation invariance, is the three-body Hamiltonian [14]:

$$\delta F^{(B)} = \frac{1}{2}\kappa_\perp\sum_{\langle ijk\rangle}(\delta\Theta_{ijk})^2 = \frac{1}{2}\kappa_\perp\sum_{\langle ijk\rangle}|(\mathbf{u}_{ij}\times\hat{\mathbf{R}}_{ij}$$
$$- \mathbf{u}_{ik}\times\hat{\mathbf{R}}_{ik})\cdot(\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik})/|\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik}||^2 \qquad (2.12)$$

where $\kappa_\perp$ is the local BB stiffness: $\kappa_\perp \equiv \partial^2 F/\partial\Theta_{ijk}^2|_{\{R\}}$. Again, following the Cauchy–Born approach of [6] and averaging over all possible strained configurations one can write

$$|\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik}|\overline{\delta\Theta_{ijk}} = (\overline{\mathbf{u}_{ij}}\times\hat{\mathbf{R}}_{ij} - \overline{\mathbf{u}_{ik}}\times\hat{\mathbf{R}}_{ik})\cdot(\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik}), \qquad (2.13)$$

which, in component notation and after expanding in the displacement field, is

$$|\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik}|\overline{\delta\Theta_{ijk}} \simeq (R_{ij}^{-1}R_{ij}^\alpha\partial_\alpha\varepsilon_{\beta\delta\gamma}u_\delta R_{ij}^\gamma - R_{ik}^{-1}R_{ik}^\chi\partial_\chi$$
$$\times \varepsilon_{\beta\eta\lambda}u_\eta R_{ik}^\lambda)\varepsilon_{\beta\mu\nu}R_{ij}^\mu R_{ij}^\nu. \qquad (2.14)$$

As shown in the appendix, one has that

$$(\overline{\mathbf{u}_{ij}}\times\hat{\mathbf{R}}_{ij})\cdot(\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik}) \simeq 2[(\mathbf{R}_{ij}^T\cdot\mathbf{e})\times\hat{\mathbf{R}}_{ij}]\cdot(\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik}). \qquad (2.15)$$

Thus, the disorder-averaged change in the interaction angle can be written as

$$\overline{\delta\Theta_{ijk}} \simeq 2[(\mathbf{R}_{ij}^T\cdot\mathbf{e})\times\hat{\mathbf{R}}_{ij} - (\mathbf{R}_{ik}^T\cdot\mathbf{e})\times\hat{\mathbf{R}}_{ik}]\cdot(\hat{\mathbf{R}}_{ij}$$
$$\times \hat{\mathbf{R}}_{ik})/|(\hat{\mathbf{R}}_{ij}\times\hat{\mathbf{R}}_{ik})| \qquad (2.16)$$

which, by making use of Lagrange's identity and rearranging terms, becomes

$$\overline{\delta\Theta_{ijk}} \simeq 2(\sin\Theta_{ijk})^{-1}\{[(\mathbf{R}_{ij}^T\cdot\mathbf{e})\cdot\hat{\mathbf{R}}_{ij} + (\mathbf{R}_{ik}^T\cdot\mathbf{e})\cdot\hat{\mathbf{R}}_{ik}]$$
$$\times \cos\Theta_{ijk} - [(\mathbf{R}_{ij}^T\cdot\mathbf{e})\cdot\hat{\mathbf{R}}_{ik} + (\mathbf{R}_{ik}^T\cdot\mathbf{e})\cdot\hat{\mathbf{R}}_{ij}]\} \qquad (2.17)$$

and, finally,

$$\overline{\delta\Theta_{ijk}} \simeq 2(R_0\sin\Theta_{ijk})^{-1}\{\cos\Theta_{ijk}[\text{Tr}(\mathbf{R}_{ij}\otimes\mathbf{R}_{ij})$$
$$+ \text{Tr}(\mathbf{R}_{ik}\otimes\mathbf{R}_{ik})]\cdot\mathbf{e} - [\text{Tr}(\mathbf{R}_{ik}\otimes\mathbf{R}_{ij})$$
$$+ \text{Tr}(\mathbf{R}_{ij}\otimes\mathbf{R}_{ik})]\cdot\mathbf{e}\}. \qquad (2.18)$$

For a pure shear, the above expression reduces to

$$\overline{\delta\Theta_{ijk}} \simeq 4(R_0\sin\Theta_{ijk})^{-1}\{[(R_{ij}^x R_{ij}^y + R_{ik}^x R_{ik}^y)\cos\Theta_{ijk}]$$
$$- [R_{ij}^y R_{ik}^x + R_{ij}^x R_{ik}^y]\}e_{xy}. \qquad (2.19)$$

We now take the isotropic average over Θ_{ijk}, thus assuming a flat distribution for Θ_{ijk}: this assumption may be realistic for systems with strong spatial disorder such as, for example, emulsion glasses, colloidal or atomic (metallic and semiconductor) glasses without directional interactions. For molecular network glasses, however, Θ_{ijk} will rather be distributed according to the chemistry of the system. With covalent network glasses, usually the number of angles Θ_{ijk} is finite and dictated by the valence, thus giving rise to distinct terms in the expansion. Application of this model to specific covalent glasses may be the object of future work. Here we limit our analysis to the case of strong disorder, so that an unbiased average yields

$$\langle\overline{\delta\Theta_{ijk}}\rangle_\Theta \simeq \langle 4(R_0\sin\Theta_{ijk})^{-1}\{[(R_{ij}^x R_{ij}^y + R_{ik}^x R_{ik}^y)\cos\Theta_{ijk}]$$
$$- [R_{ij}^y R_{ik}^x + R_{ij}^x R_{ik}^y]\}\rangle_\Theta e_{xy} \simeq \frac{4}{3}R_0\sin\varphi\cos\varphi$$
$$\times (-\sin^2\theta + \cos^2\theta - 4\sin\theta\cos\theta)e_{xy} \qquad (2.20)$$

where $R_{ik}^x = \sin(\theta + \Theta)\cos\varphi$ and $R_{ik}^y = \sin(\theta + \Theta)\sin\varphi$ have been used. As before, we assume random orientation of the bonds in the reference state $\{R\}$ so that, on average, each term in the summation in equation (2.12) contributes

$$\langle \langle \overline{\delta \Theta_{ijk}} \rangle_\Theta^2 \rangle_\Omega \simeq \frac{16}{9} R_0^2 \left[\frac{1}{4\pi} \int \int d\varphi \sin\theta \, d\theta (\sin\varphi \cos\varphi)^2 \right.$$
$$\times (\sin^4\theta + \cos^4\theta + 14\sin^2\theta\cos^2\theta$$
$$\left. + 8\sin^3\theta\cos\theta - 8\sin\theta\cos^3\theta) \right] e_{xy}. \qquad (2.21)$$

Therefore, using $\overline{\delta\Theta_{ijk} - \overline{\delta\Theta_{jk}}}^2 \ll \overline{\delta\Theta_{ijk}}^2$ for the average over disorder, as well as $\langle \delta\Theta_{ijk} - \langle \delta\Theta_{ijk} \rangle_\Theta \rangle_\Theta^2 \ll \langle \delta\Theta_{ijk} \rangle_\Theta^2$ for the spatial average over the bending angle, linear elasticity leads to

$$G^{(B)} \simeq \frac{124}{135\pi} \kappa_\perp z^{(B)} \phi R_0^{-1} \qquad (2.22)$$

where the sum over three-body interactions has been replaced by $\frac{1}{3} z N / V \equiv 2 z \phi / \pi R_0^3$.

In equations (2.11) and (2.22) the definition of the microscopic bond rigidities ($\kappa_\parallel$ and $\kappa_\perp$, respectively) is clearly different and the numerical prefactor is also different. In the BB case, the value of the prefactor is especially important, because for (real) network glasses it also contains information about the chemistry-dependent geometry of the network. Here, the prefactor $(124/135)\pi^{-1}$ has been found for the case of nondirectional bonds and strong disorder but, in the case of real covalent glasses, it depends on the values of the bond-bending angle Θ_{ijk}. For a generic system where both CF and BB interactions are present, as in many real glasses, the shear modulus can be estimated from the stress–strain relation $\sigma_{\alpha\beta} \equiv \partial \delta F / \partial e_{\alpha\beta}$, where according to Cauchy–Born theory $\delta F \simeq \delta F^{(C)} + \delta F^{(B)}$, as

$$G = G^{(C)} + G^{(B)} \simeq \left(\frac{4}{5\pi} \kappa_\parallel z^{(C)} + \frac{124}{135\pi} \kappa_\perp z^{(B)} \right) \phi R_0^{-1} \qquad (2.23)$$

$G^{(C)}$ and $G^{(B)}$ represent, respectively, the values to which the shear modulus would reduce in the case where respectively purely central interactions and purely bond-bending interactions have to be considered in the free energy.

Equation (2.23) accounts for the fact that the mean number of bonds per particle which display BB resistance may differ from that of purely CF bonds. Indeed, for real covalent glasses, $z^{(B)}$ is a function of the valence which, in turn, is determined by the specific chemistry of the glass under consideration.

3. Discussion and potential applications

Equation (2.23) has been derived by systematically applying Cauchy–Born theory (with the expansion written in terms of the *relative* deviations) and gives the macroscopic elastic response to the shear of amorphous solids with both central-force and bond-bending interactions as a function of coarse-grained parameters. These are the mean coordination (z), the volume fraction (ϕ), the interparticle interactions (embedded in the Born–Huang term κ) and the mean separation distance (R_0) between nearest neighbours in the reference (stressed)

configuration. The latter, in a solid, is approximately equal to the diameter of the building blocks. We would like to clarify, at this point, the differences of the approach outlined in this work as compared to the various models in the literature, especially within rheological models. In most of these cases, the heterogeneous and heuristic character of the assumptions leads to numerical prefactors inconsistent with each other and generally not quantitatively comparable with the experiments [15]. Moreover, the affine approximation is sometimes applied to weakly bonded materials where nonaffine rearrangements are important instead. Including bond-bending terms in the expansion as done here is crucial, thus making possible the application of continuum theory to such materials as strong covalent glasses (Si, Ge) where nonaffine rearrangements are smaller [9].

Furthermore, equation (2.23) tells us that the shear modulus of glasses is sensitive to an increase in the average number of covalent bonds (i.e. bonds which can react to shear forces) per atom. Increasing the average number of covalent bonds per atom has two main consequences on the properties of a glass: the stabilization of soft (localized) transverse vibrations and the shift of the Ioffe–Regel crossover to higher frequencies. Hence, both these effects are expected to translate into a decrease of the well-documented excess of modes in the vibrational density of states of glasses, i.e. a decrease in the intensity of the so-called boson peak [16]. Experimentally, a situation where the average number of covalent bonds per atom can be varied (within the range $2 \leqslant z^{(B)} \leqslant 4$) is found in chalcogenide alloys $Ge_x Se_{1-x}$, where x represents the relative concentration of Ge by varying which the average number of covalent bonds per atom can be varied [17]. It was indeed found experimentally that the boson peak intensity decreases upon increasing x, thus $D(\omega_{BP})/\omega_{BP} \propto 1/x^\beta$, where β is an exponent of order 1 [18]. According to our result, equation (2.23), $G \propto x$. Assuming that this holds even when nonaffinity is important, it follows that $D(\omega_{BP})/\omega_{BP} \propto 1/G^\beta$. The latter relation with $\beta = 1$ has been proposed on the basis of simulations of 2D spin glasses in recent work [19].

3.1. Aggregated colloidal systems

We should note that equation (2.23) may also find application in better understanding the structure–elasticity properties of (dense) aggregated colloidal systems. In fact, it has been recently shown that polymer latex particles in the micron range display BB rigidity as a consequence of contact adhesion [20, 21]. Therefore, for such colloidal systems, the BB stiffness in equation (2.22) may be expressed as a function of the surface adhesion parameters according to the experimental findings of [20] where the relation $\kappa_\perp \simeq 6\pi a_c^4 E_0 / R_0^3$ was proposed (a_c is the radius of the contact area of adhesion between two particles and E_0 is the particle Young's modulus). This is motivated by recognizing that the microscopic elastic constant for shear rigidity, $\kappa_\perp$, is defined here as the energy cost for changing the angle between two bonds with a vertex in common, in the same way as in previous studies on colloidal gels and aggregates, see, for example, [20] and [22]. It is therefore consistent, also

from a dimensional point of view, with the single-bond BB rigidity measured in [20]. In particular equation (2.23) tells us that the presence of bond-bending forces gives an important contribution to the global shear rigidity. In the case of a colloidal aggregated state with $z^{(B)} = z^{(C)} = 3$ for example, the system is largely overconstrained (since the number of saturated degrees of freedom is $z^{(C)}/2 + z^{(B)}(z^{(B)} - 1)/2 = 9$) and nonaffine displacements are small. Thus, our model is expected to be particularly accurate. Situations where $z^{(B)} = z^{(C)} \approx 3$ or larger are commonly encountered in not too diluted aggregated or gelled colloidal dispersions (see, e.g., [23–25]). Thus, combining the results of the present work with those of [20] for the microscopic description of bond-bending rigidity, may help in future work to lay down the groundwork for a comprehensive quantitative modelling of the elastic properties of aggregated colloidal systems in the semi-dilute to concentrated regime.

4. Conclusions

The systematic Cauchy–Born approach to amorphous solids, in the same spirit of [6], has been applied to evaluate the macroscopic response to shear of low-T glassy states of spherical particles interacting via a central pair interaction potential supplemented with an angular (bond-bending) three-body interaction term. Expressions in closed form are derived by making use of the affine approximation. The latter is generally a strong assumption when dealing with disordered systems, but may lead to small errors if the interparticle bonds can support significant bending moments (thus greatly reducing the number of degrees of freedom), as in covalent glasses (e.g. amorphous Si and Ge) [9]. Further, the model has the potentiality to account for the specific chemistry-dependent structure of real glasses. In the case of purely *central* pair interaction potentials, the situation is more complex because nonaffine relaxations are usually important. The affine approximation, therefore, is of limited application. However, also in the latter case, as shown elsewhere [11], the formulae derived here can nevertheless yield accurate predictions for colloidal glasses in the limit of strong short-ranged interparticle attraction. In this limit, the observed linear elastic regime is indeed due to stretching of the bonds [13, 26], so that, the particles being localized upon strain within the short range of attraction, the assumptions used here yield reasonable predictions.

Acknowledgments

Appendix. Derivation of equation (2.15)

One can decompose the gradient expansion of the smooth displacement field $\mathbf{u}(\mathbf{r})$ into an explicitly symmetric part (i.e. the disorder-averaged symmetric strain tensor) and an antisymmetric one as

$$\overline{\mathbf{u}_{ij}} \equiv \overline{\mathbf{u}_i - \mathbf{u}_j} \simeq (\mathbf{R}_{ij} \cdot \nabla)\mathbf{u} = [\mathbf{R}_{ij}^{\mathrm{T}} \cdot \mathbf{e} + \tfrac{1}{2}(\nabla \times \mathbf{u}) \times \mathbf{R}_{ij}]. \tag{A.1}$$

Using the well-known identities

$$(\nabla \times \mathbf{u}) \times \mathbf{R}_{ij} = -\mathbf{R}_{ij} \times (\nabla \times \mathbf{u}) = -\nabla(\mathbf{R}_{ij} \cdot \mathbf{u}) + (\mathbf{R}_{ij} \cdot \nabla)\mathbf{u}. \tag{A.2}$$

Equation (A.1) can be rewritten as

$$\overline{\mathbf{u}_{ij}} \simeq (\mathbf{R}_{ij} \cdot \nabla)\mathbf{u} = [\mathbf{R}_{ij}^{\mathrm{T}} \cdot \mathbf{e} - \tfrac{1}{2}\nabla(\mathbf{R}_{ij} \cdot \mathbf{u}) + \tfrac{1}{2}(\mathbf{R}_{ij} \cdot \nabla)\mathbf{u}]. \tag{A.3}$$

Rearranging terms:

$$\overline{\mathbf{u}_{ij}} \simeq (\mathbf{R}_{ij} \cdot \nabla)\mathbf{u} = 2[\mathbf{R}_{ij}^{\mathrm{T}} \cdot \mathbf{e} - \tfrac{1}{2}\nabla(\mathbf{R}_{ij} \cdot \mathbf{u})]. \tag{A.4}$$

Hence, we can rewrite equation (2.16) as

$$(\overline{\mathbf{u}_{ij}} \times \hat{\mathbf{R}}_{ij}) \cdot (\hat{\mathbf{R}}_{ij} \times \hat{\mathbf{R}}_{ik}) \simeq 2\{[(\mathbf{R}_{ij}^{\mathrm{T}} \cdot \mathbf{e}) \times \hat{\mathbf{R}}_{ij}]$$
$$- \tfrac{1}{2}[\nabla(\mathbf{R}_{ij} \cdot \mathbf{u}) \times \hat{\mathbf{R}}_{ij}]\} \cdot (\hat{\mathbf{R}}_{ij} \times \hat{\mathbf{R}}_{ik}). \tag{A.5}$$

For the antisymmetric parts, we can use the identity $\nabla(\mathbf{R}_{ij} \cdot \mathbf{u}) \times \hat{\mathbf{R}}_{ij} = \nabla \times (\mathbf{R}_{ij} \cdot \mathbf{u})\hat{\mathbf{R}}_{ij} - (\mathbf{R}_{ij} \cdot \mathbf{u})\nabla \times \hat{\mathbf{R}}_{ij}$, where the second term on the rhs is clearly zero. Therefore, the term $[\nabla \times (\mathbf{R}_{ij} \cdot \mathbf{u})\hat{\mathbf{R}}_{ij}] \cdot (\hat{\mathbf{R}}_{ij} \times \hat{\mathbf{R}}_{ik})$, making use of Lagrange's identity, is seen to be zero:

$$[\nabla \times (\mathbf{R}_{ij} \cdot \mathbf{u})\hat{\mathbf{R}}_{ij}] \cdot (\hat{\mathbf{R}}_{ij} \times \hat{\mathbf{R}}_{ik})$$
$$= (\nabla \cdot \hat{\mathbf{R}}_{ij})[(\mathbf{R}_{ij} \cdot \mathbf{u})\hat{\mathbf{R}}_{ij} \cdot \hat{\mathbf{R}}_{ik}]$$
$$- (\nabla \cdot \hat{\mathbf{R}}_{ik})[(\mathbf{R}_{ij} \cdot \mathbf{u})\hat{\mathbf{R}}_{ij} \cdot \hat{\mathbf{R}}_{ij}] = 0 \tag{A.6}$$

because $\hat{\mathbf{R}}_{ij}$ and $\hat{\mathbf{R}}_{ik}$ are constant vectors. Hence, equation (2.15) is verified.

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