Vibrations of amorphous nanometric structures: when does the classical continuum theory apply?

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Abstract

We present in this paper an extensive study of the size dependence of the low-frequency vibrational eigenmodes of two- and three-dimensional amorphous (non-crystalline) nanoparticles. We show that classical continuum elasticity (Lamb modes) breaks down when the wavelength of the solicitation is smaller than a characteristic length of approximately 40 atomic sizes. This length is related to the presence of additional vortices in the atomic displacement field of the nanoparticle. These vortices are related to local anisotropy in the inhomogeneous elastic moduli of the amorphous structure. We show how they affect the average mechanical response of the nanoparticles.

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1. Introduction

In today’s materials sciences, the increasing development of materials containing nanometric size structures naturally leads one to question the limits of applicability of the classical continuum elasticity theory, which is in principle valid only at length scales much larger than the interatomic distance [1–3]. Investigating the vibration modes of nanometric objects using atomic level simulations is a natural way of probing this applicability. Such an investigation is particularly relevant from an experimental viewpoint, since these properties, inferred from spectroscopic measurements, are systematically interpreted within the framework of continuum elasticity [4–7]. It has been shown for metallic clusters, for example, that the low-frequency classical Lamb modes [8] for spherical clusters seems to be valid down to nanometric lengthscales. However, for macroscopic but amorphous materials, there is an anomalous density of states in the THz range (the so-called Boson peak) [9–11], leading to an anomalous temperature dependence of the heat capacity in such materials.

In this paper, we investigate the size dependence of the low-frequency vibrational eigenmodes of amorphous nanoparticles. Although metallic clusters of more than 20 molecular sizes are now known to be crystalline in the usual conditions of preparation [12], the existence of non-crystalline nanoparticles is a matter of fact. It has been shown, for example, by Hoareau et al. [13], that small deposited antimony particles on graphite surface are amorphous and...
becomes crystalline only for a given deposits density. Crystalline–amorphous phase transformation may also occur with temperature change, as in Si deposited clusters [14]. Finally, clusters with hybride bonds, such as clusters of Bore, present a lot of possible metastable states such as amorphous. We focus here on amorphous clusters; the case of crystalline clusters has been studied by Saviot et al. [15].

2. Sample preparation and characterization

The objects we consider are either disk-shaped clusters of diameter $2R$ (Fig. 1), or bulk-like systems contained in a square of side $L$ with periodic boundary conditions. Computationally, they are formed by quenching very quickly a slightly polydisperse liquid of spherical particles interacting via simple Lennard–Jones pair potentials, into the nearest energy minimum, following a fixed protocol [19,20] using standard molecular dynamics, steepest descent and conjugate gradient methods [16,17]. For the clusters, the quench is realized after cutting a sphere (or a disk in 2D) out of a much larger bulk sample. The resulting structures are amorphous, i.e. they exhibit not a crystal-like, but a liquid-like order. The density of the bulk-like materials corresponds to a near zero pressure state, while that of the clusters slightly depends on their radius.

We have been able to analyse systems containing 50–40,000 particles, with a density close to 1. This corresponds to sizes ranging from $R = 2.3\sigma$ to $40\sigma$ in 3D, and from $R = 4\sigma$ to $200\sigma$ in 2D, where $\sigma$ is the average particle diameter ($\sigma = 1 \pm 0.05$). We have checked in the spatial correlation function of forces and positions (Fig. 2) that such systems do not display any visible characteristic length, other than the average particle diameter. They are however strongly inhomogeneous, with a large distribution of quenched forces and stresses (Fig. 3). We will show how the disorder affects at small scales the acoustical response of the system.

Fig. 1. Representation of the force network frozen in a large, amorphous Lennard–Jones cluster ($2R \approx 30$). Atoms lie at the vertices, and bonds represent the interaction forces. The line scale is proportional to the magnitude of the associated force. Grey lines represent tensile forces, and black lines indicate repulsive forces.
3. Vibration modes of amorphous nanoparticles

In a computer-simulated system, in which all particle coordinates and interparticle forces are exactly known, it is possible to calculate exactly the vibration frequencies around an equilibrium position. This is achieved by the exact diagonalization of the so-called dynamical matrix \[ (DN) \times (DN) \] (where \(D\) is the number of spatial dimensions and \(N\) the number of particles) matrix expressible in terms of the first and second derivatives of the interparticle interaction potentials. The corresponding displacement fields are given by the eigenvectors of the dynamical matrix. We have carried out \[ [19,20] \] a systematic comparison of the exact eigenfrequencies calculated in this way with those predicted by classical continuum elasticity \[ [2,8] \]. We concentrate on the lowest end of the vibrational spectrum, since this is the part that corresponds to the largest wavelengths for the vibrations. Hence, the corresponding modes are those for which one would expect the continuum theory to be applicable. They are also those which are probed in low-frequency Raman scattering experiments \[ [4] \], in order to determine the typical size of nanoparticles.

In case of spherical or disk-shaped aggregates, the classical eigenfrequencies \[ [8,19] \] are characterized by two quantum numbers \(n\) and \(k\). They are of the form \(\omega_n = \frac{2}{\pi} \frac{c_T}{\rho} \sqrt{n(n+1)}\), where \(c_T\) is the transverse sound velocity, \(c_T = \sqrt{\mu/\rho}\), \(\rho\) the mass density, \(\mu\) the shear modulus and \(\nu\) the Poisson ratio of the material. For 2D systems and \(n > 0\), each mode exhibits a two-fold degeneracy, corresponding to oscillations in two orthogonal directions. Degenerate eigenvalues are also present in 3D systems, due to the high (spherical) symmetry of the continuum treatment. In the latter case, the eigenmodes are given by Bessel functions and spherical harmonics, with the degeneracy \((n+1)\).

The exact numerical results show that the degeneracy of eigenvalues is recovered only for large enough system sizes, typically \(R > 40\sigma\). Moreover, for 2D systems, the convergence of the eigenfrequency to its theoretical value (Fig. 4), with the numerical value of the macroscopic elastic moduli measured independently in an elongation experiment (see Section 4.2), is effective only for system sizes larger than \(40\sigma\), even for the lowest frequency. The convergence appears even later for higher modes. For 3D systems, the convergence to the theoretical values has not been reached for the largest systems \((R \approx 40\sigma)\), we have studied.
Our results thus indicate clearly the existence of a mesoscopic size \( R \approx 40\sigma \) below which the predictions of classical continuum elasticity becomes erroneous, for 2D as well as for 3D amorphous nanoparticles. In order to understand these results, we have analysed the mechanical properties of the bulk phase.

4. Mechanical properties of the bulk phase

The analysis of the periodic bulk phase allows us to study various mechanical solicitations on very large systems, independently of the large surface over volume ratio present in nanoparticles. Moreover, the response of the system is then easy to analyse because of its simple symmetry.
4.1. Vibration modes

For bulk-like systems with periodic boundary conditions, the vibration modes are analysed in the same way as for the clusters. The eigenmodes are now plane waves. For 2D systems, the theoretical frequencies are thus of the form \( \omega_{mn} = \frac{2\pi}{Lc}\sqrt{n^2 + m^2} \), with \( c \equiv c_T \) for the transverse waves, and \( c \equiv c_L \) for the longitudinal waves. The results are qualitatively the same as for the clusters (Fig. 5); the characteristic fourfold (or eightfold if \( n \neq m \neq 0 \)) degeneracy, associated with waves travelling in two opposite and orthogonal directions, is recovered only for large enough system sizes \( (L > 40\sigma) \). In this case it is also possible to draw the rescaled eigenfrequencies \( \omega/\omega_{mn} \) versus wavelength \( \lambda \equiv L/(n^2 + m^2)^{1/2} \). Fig. 6 shows that the crossover to continuum theory occurs at a critical wavelength \( \lambda_c \approx 40\sigma \) for all modes. Moreover the eigenvectors display additional vortices, even for the lowest frequency. The size of the vortices is determined by the correlation function of the displacement field. It is approximately \( \xi \approx 40\sigma \), and is independent on the wavelength \( \lambda \). The wavelength dependence \( \propto 1/\lambda^2 \) of the amplitude of the noise \( \delta u \) in the displacement field can be explained [19] in terms of diffusion of acoustic modes on the rotational structure of characteristic size \( \xi \). Note that similar vortices are also present in the anomalous acoustic response of 2D nanoparticles. We see clearly in the bulk phase, that they do not depend on the size of the system.

4.2. Elongation and shear

The same kind of additional vortices in the displacement field (non-affine component of the displacement field) appears also in a shear experiment in 2D systems, or in a simple elongation (Fig. 7). In this case, a large sample \( (N = 10,000; L = 104\sigma) \) is submitted first to a homogeneous strain \( (\epsilon_{xx} = \text{cste}, \epsilon_{xy} = \text{cste}) \) and then relaxes with fixed boundary conditions. The resulting displacement field is computed after relaxing the atoms to their new equilibrium positions. We have

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Fig. 7. Non-affine component \( \delta u(x, y) \) of the displacement vector field, under elongation in \( x \) direction. The theoretical displacement (affine component proportional to the homogeneous strain) has been subtracted, in this figure.
chosen the imposed strain sufficiently weak, in order to induce reversible (elastic) rearrangements. The energy stored in the rotational structures is, in this case, of the same order as the total mechanical energy, as it can be inferred from the comparison between the measured average stress and the stress obtained assuming only that the response is affine [19]. This last result explains why the elastic shear modulus measured in an amorphous system is approximately twice smaller than the shear modulus of the corresponding crystal [19,21,22].

4.3. Response to a point force

The analysis of the mechanical elastic response of the bulk-like system to a point force shows analogous results [23]. The reversible displacement field obtained in this case after relaxing the system to its new equilibrium position (Fig. 8) displays additional vortices of mesoscopic size, close to the position of the point source. Such a transverse additional motion of the particles can be explained only by local anisotropy in the local elastic moduli, and disappears in ordered (crystalline) systems. In this case, a perturbative calculation [23] shows that the size of the vortices scales as $\xi \approx d(\mu/\Delta\mu)$, where $d$ is the distance between the defects and $\Delta\mu$ is the variance of the local shear modulus $\mu$.

5. Conclusion

We have shown that the application of classical continuum elasticity theory is subject to strong limitations in amorphous nanometric structures, below a length scale $\xi$ of typically 40 interatomic distances. This effect is particularly important when the
wavelength of the vibrational excitation (or the size of
the nanoparticle) is less than this characteristic size $\xi$.
The origin of the departure from classical behavior is
very likely related to the disorder in interatomic
interactions (local stresses, inhomogeneities in elastic
constants, local anisotropy). This is revealed by the
investigation of the non-affine part of the displacement
field when a large (bulk-like) sample is deformed.
Transversal motion of the particles gives rise to large
vortices of size $\xi$. This leads to an important decrease
of the average shear modulus in amorphous systems
compared with the corresponding crystals. Interestingly,
similar sizes are often invoked [24], as typical
of the heterogeneities that give rise to anomalies in the
vibrational properties of disordered solids (glasses) in
the terahertz frequency domain, the so-called Boson
peak. In particular, [24] considers the existence of
rigid domains separated by softer interfacial zones, not
unlike those revealed by the non-affine displacement
pattern of Fig. 7. Our work offers a new vantage point
on this feature: at the wavelength corresponding to
these THz vibrations, comparing the vibrational den-
sity of states to that of a continuum elastic model is not
necessarily meaningful. It also suggests the existence
of domains where damage, and thus fragmentation,
could be localized. Note that the typical size $\xi$ depends
on the density, and we are now investigating more
precisely its pressure dependence, in relation with
experimental investigations [10,11]. In the future,
we will explore the behavior of the structure, beyond
the elastic regime.

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