Vibrations of amorphous, nanometric structures: When does continuum theory apply?

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PACS. 72.80.Ng – Disordered solids.
PACS. 65.60.+a – Thermal properties of amorphous solids and glasses.
PACS. 61.46.+w – Nanoscale materials: nanoparticles.

Abstract. – We investigate the low frequency end of the vibrational spectrum in small (nanometric) disordered systems. Using numerical simulation and exact diagonalization for simple two dimensional models, we show that continuum elasticity, applied to these systems, actually breaks down below a length scale of typically 30 to 50 molecular sizes. This length scale is likely related to the one which is generally invoked to explain the peculiar vibrational properties of glassy systems.

Determining the vibrational properties — i.e. the vibration frequencies and the associated displacement fields — of solid bodies with various shapes is a well studied area of continuum mechanics. The early works of Lamb or Rayleigh \(\text{[1]}\), who determined these vibrations using classical elasticity theory of isotropic materials, have found applications in fields as different as planetary science and nuclear physics. In today’s materials sciences, the increasing development of materials containing nanometer size structures naturally leads one to question the limits of applicability of the continuum elasticity theory, which is in principle valid only on length scales much larger than the interatomic distances \(\text{[2, 3]}\). 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 \(\text{[4–6]}\). In this paper, we use a simple model, which is commonly used as a generic model for liquids and amorphous \(\text{[7]}\) solids, to investigate the applicability of continuum theory at small scales.

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 exact diagonalization of the so called dynamical matrix \(\text{[8]}\), a \((dN) \times (dN)\) (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

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Fig. 1 – Eigenfrequencies for disk shaped clusters. Squares of the eigenfrequencies, versus diameter $2R$, for the lowest frequency vibration modes of disk shape clusters of increasing sizes. Each symbol corresponds to a different mode number $p$. The value of $p$ is indicated for each series of black symbols (even values of $p$). The first nontrivial mode corresponds to $p = 4$, since the first three modes correspond to global translations and rotation. The frequencies have been multiplied by the size and by the sound velocity, so that in the limit of large systems they should regroup into degenerate pairs and tend to a constant value. These quantized values can be calculated explicitly from the theory of elasticity (horizontal lines). The quantum numbers $(k, n)$ associated to each of these eigenmodes within elastic theory are also indicated.

The dynamical matrix. We have carried out a systematic comparison of the exact eigenfrequencies calculated in this way with those predicted by continuum elasticity, for two dimensional $(d=2)$ objects of increasingly large sizes. The objects we consider are either disk shaped clusters of diameter $2R$, or bulk like systems contained in a square of side $L$ with periodic boundary conditions. Microscopically, they are formed by quenching a slightly polydisperse liquid of spherical particles interacting via simple Lennard-Jones pair potentials into the nearest energy minimum. For the clusters, the quench is realized after cutting a disk out of a much larger bulk like sample. The resulting structures are amorphous, i.e. exhibit no crystal like order.

We have generated such two dimensional amorphous clusters with sizes ranging from $R = 3\sigma$ to $R = 109\sigma$, where $\sigma$ is the particle diameter. This corresponds to numbers of atoms between $N = 16$ and $N = 32768$. A comparable range has been studied for the bulk like materials, with $7 < L/\sigma < 208$ and $50 < N < 40000$. The density of the bulk like materials corresponds to a near zero pressure state, while that of the clusters slightly depends on their radius. A smaller radius implies a higher capillary pressure, therefore a slightly higher density. For each system, the lowest (100 first) vibration eigenfrequencies and eigenvectors have been determined using the version of the Lanczos method implemented in the PARPACK numerical package \cite{PARPACK}. 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 continuum theory to be applicable. They are also those which are probed in low frequency Raman scattering experiments \cite{Raman}, in order to...
Once the exact modes are determined, they may be compared to those obtained from the continuum elasticity theory. For bulk like systems with periodic boundary conditions, these elastic modes are simply plane waves, and the eigenfrequencies are quantized by two integers \((n, m)\) that define the periodicities in the \(x\) and \(y\) directions, respectively. The plane waves may be transverse, with a displacement field orthogonal to the direction of propagation, or longitudinal, with the displacement parallel to this direction. Quantitatively, the frequencies of the transverse waves are of the form \(\omega_{nm} = \frac{2\pi}{L} c_T \sqrt{n^2 + m^2}\), where \(c_T\) is the transverse sound velocity. A similar formula is obtained for longitudinal waves, with a velocity \(c_L > c_T\). Hence the eigenfrequency associated with a pair of different integers \(n, m\) has a four-fold (or eight-fold if \(n \neq m \neq 0\)) degeneracy, associated with waves travelling in two opposite and orthogonal directions. The longitudinal and transverse sound velocities can be expressed in terms of the Lamé coefficients \(\lambda\) and \(\mu\) \(\[2\] \): \(c_T = \sqrt{\mu/\rho}\) and \(c_L = \sqrt{(\lambda + 2\mu)/\rho}\), where \(\rho\) is the mass density.

The situation for disk-shaped objects is somewhat more complex, with again each vibration characterized by two quantum numbers \(n\) and \(k\), and eigen-frequencies of the form \(\omega_n = \frac{2\pi}{R} c_T f_{nk}(\nu)\). Here \(\nu\) is the Poisson ratio of the material. The quantum number \(n\) is associated with the angular dependency of the displacement field, and the number \(k\) to its radial dependency. For \(n > 0\), each mode exhibits a twofold degeneracy, corresponding to oscillations in two orthogonal directions. Degenerate eigenvalues are therefore inherent to the continuum treatment of systems which are assumed to be highly symmetric.

Figures 1 and 2 present the results of the comparison between elastic theory predictions and exact diagonalization for the eigenvalues, for systems of variable sizes. Elastic theory would predict that \(\omega L\) \((2\omega R\) for clusters\) values are independent of the size, and highly degenerated. The figures show that this characteristic degeneracy is recovered only for large...
Fig. 3 – Schematic representation of the displacement fields associated to some low frequency modes in a large, disk-shaped cluster with 10000 particles ($2R = 120$). For such large clusters, the displacement fields essentially conform to standard elastic behavior. The two quantum numbers $k$ and $n$ are indicated for each mode. The twofold degeneracy, corresponding to displacements fields rotated by 90 degrees, is illustrated in the first six fields. The last two correspond to modes with $n = 0$, and their frequency is not degenerated. Note that the last mode represented is a 'breathing' mode, with a relatively high frequency (the 15th by increasing magnitudes).

The elastic limits are obtained from the analytic formulae described above, by inserting the appropriate values of the Lamé coefficients. These values in turn are determined numerically, from the changes in energy associated with a small compression (or shear deformation) of a large, bulk sample. The structure of the displacement fields for some of the lowest eigenmodes of a large cluster ($R = 60$) is shown in figure 3.

Our results clearly indicate the existence of a typical size, $L \simeq 40 \sigma$, below which the predictions of continuum elasticity become erroneous. The classical degeneracy of the vibration eigen-frequencies is lifted, and the resulting density of states, when averaged over many realizations (typically 20), becomes a continuous function. Figures 1 and 2 show that the approach of the elastic limit is nonmonotonous, with systems of intermediate sizes having eigenfrequencies lower than predicted by the elastic theory, while very small systems vibrate at higher frequencies.

It is therefore interesting to speculate on the nature of the microscopic features that become relevant on this length scale, and make the elastic approach inappropriate. Density variations are easily excluded, since the density is always found to be perfectly homogeneous down to a scale typical of the interatomic separation. An interesting alternative is to look for inhomogeneities in the local stresses at the atomic scale, which could lead to local anisotropies responsible for the lifting the elastic degeneracy. Note that although the system is lying in an
energy minimum, its disordered character implies that the forces between pairs of neighboring particles are, as a rule, nonzero, so that local stresses are frozen into each sample.

A pictorial representation of these stresses is given in figure 4 which shows the network of repulsive (black) and attractive (red) forces in a large, disk-shaped cluster. These stresses are widely distributed. Visual inspection reveals a characteristic length scale of the repulsive forces network, much larger than the interatomic separation. Interestingly, the figure also reveals the existence of 'force chains' very similar to those found in granular media under stress [10]. This feature may be added to the list of similarities which have been noticed between granular and amorphous (glassy) materials [11]. Note, however, that the existence of an elastic limit for large systems, which is clearly established here for amorphous systems, is still a matter of debate in granular systems [12].

Another way of illustrating the failure of classical elasticity at small scales is to investigate the displacement field in a large, deformed sample. If the system is uniformly strained at large scales (e.g. by compressing a rectangular box), classical elasticity implies that the strain is uniform at all scales, so that the atomic displacement field should be affine with respect to the box deformation. We have investigated the nonaffine component of the atomic displacement field in large systems subjected to a compression, and found that the 'elastic length' discussed above manifests itself through correlated deviations from a purely affine displacement. In some regions, the displacement is much larger than expected from a purely affine transformation, as illustrated in figure 5. The size of these regions is similar, albeit somewhat smaller, than the one at which the results of continuum elasticity for the vibration modes are recovered.

An important consequence of the existence of these "softer" regions is that the Lamé
Fig. 5 – Non-affine component of the displacement field. A large sample (10000 particles, \( L = 104 \)) with periodic boundary conditions has been submitted to an asymptotically weak elongational strain in horizontal direction. The resulting displacement field is computed after relaxing the atoms to their new equilibrium positions. The vector field represented on the figure is (proportional to) the non-affine part of this displacement field, i.e. the displacement from which the affine component proportional to the homogeneous strain has been substracted.

Coefficients have to be computed from the change in total energy due to the actual elastic displacement field following a deformation (an elongation in the case of figure 5). These coefficients can differ, by a factor as large as 2, from those that would result from an homogeneous deformation. The latter are obtained from standard formulae for elastic constants \( [16] \) such as

\[
\mu = \frac{1}{V} \sum_{ij} \left( \frac{\phi''(r_{ij})}{r_{ij}^2} - \frac{\phi'(r_{ij})}{r_{ij}} \right) (x_i - x_j)^2 (y_i - y_j)^2.
\]  

(1)

The derivation of equation 1, however, implicitly assumes that the deformations are affine on all scales. Using such a formula, one indeed obtains a value for \( \mu \) which is much too large to account for our results on vibrational frequencies. Clearly, a calculation taking into account the nonaffine character of the displacements is necessary for disordered systems. For such a calculation, a system size larger than the correlation length of the non-affine displacement field is needed to obtain a reliable estimate of the Lamé coefficients. Below this length scale, the local elastic coefficients are inhomogeneous. Inhomogeneities in local elastic coefficients, which are explicitly displayed in figure 5, are an essential ingredient in several recent calculations on disordered elastic systems \( [13, 14] \). Our work provides a first estimate for the typical length scale of these inhomogeneities.

Using computer generated amorphous structures, we have thus shown that the application of continuum elasticity theory is subject to strong limitations in amorphous solids, below a length scale of typically 40 interatomic distances. This length is surprisingly large, considering
the short range of the interatomic correlations. The origin of the departure from elastic behavior is very likely related to the disorder in interatomic interactions (local stresses and force constants). This disorder is illustrated by the structure of the force network frozen into the solid, as shown in figure 4. Local inhomogeneities in elastic constants are revealed by the investigation of the nonaffine part of the displacement field when a large sample is deformed, and reveal a similar length scale. Interestingly, similar, or somewhat smaller, sizes are often invoked \[15,18\], 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, reference \[18\] considers the existence of rigid domains separated by softer interfacial zones, not unlike those revealed by the nonaffine displacement pattern of figure 5. Our work offers a new point of view on this feature. At the wavelength corresponding to these THz vibrations, comparing the vibrational density of states to that of a continuum, elastic model (the Debye model) is not necessarily meaningful. It also suggests that numerical investigation of vibrational properties in disordered systems should systematically make use of large samples \((L \gg 40\sigma)\), in order to avoid finite-size effects and to include correctly contributions from “softer” elastic regions. Although we are aware that this conclusion may have to be modified in a three dimensional space, careful finite-size studies should also be undertaken in that case \[19\].

REFERENCES

[1] ERINGEN A.C. and SUHUBI E.S., Elastodynamics (Academic, New-York)1975.
[2] LANDAU L.D. and LIFSHITZ E.M., Theory of Elasticity (Butterworth-Heinemann, London)1995.
[3] ALEXANDER S., Phys. Rep., 296 (1998) 65.
[4] FATTI N.D. and VOISIN C. and CHEVY F. and VALLEE F. and FLYTZANIS C., J. Chem. Phys., 110 (1999) 11484.
[5] HODAK J.H. and HENGLEIN A. and HARTLAND G.V., J. Phys. Chem., 104 (2000) 9954.
[6] SAVIOT L. and CHAMPAGNON B. and DUVAL E. and EKIMOV A.I., Phys. Rev. B., 57 (1998) 341.
[7] Depending on the sample preparation method, nanosized particles may be in fact more or less crystalline, rather than amorphous. However, as amorphous clusters of imperfect crystallites are possible the query raised in the title is relevant.
[8] KITTEL C., Introduction to Solid State Physics ((J. Wiley, New-York)1995.
[9] CHOI J.Y. and DONGARRA J.J. and POZO R. and SORENSEN D.C. and WALKER D.W., International Journal Of Supercomputer Applications, 8 (1994) 99.
[10] CATES M.E. and WITTMER J.P. and BOUCHAUD J.P. and CLAUDIN P., Phys. Rev. Lett., 81 (1998) 1841.
[11] LIU A.J. and NAGEL S.R., Nature, 396 (1998) 21.
[12] CATES M.E. and WITTMER J.P. and BOUCHAUD J.P. and CLAUDIN P., Chaos, 9 (1999) 511.
[13] SCHIRMACHER W. and DIEZEMANN G. and GANTER C., Phys. Rev. Lett., 81 (1998) 136.
[14] ANGELANI L. et al., Phys. Rev. Lett., 84 (2000) 4874.
[15] DIANOUX A.J. and PETRY W. and RICHTER D., Dynamics of Disordered materials (North Holland, Amsterdam) 1993.
[16] SQUIRE D.R. and HOLT A.C. and HOOVER W.G., Physica, 42 (1969) 388.
[17] In this expression, \(\phi\) is the interparticle pair potential, \(\phi'\) and \(\phi''\) its derivatives, and the sum runs over all pairs of particles. The formula has been adapted from ref. \[16\] for the special case of zero temperature.
[18] DUVAL E. and MERMET I., Phys. Rev. B, 58 (1998) 8159.
[19] Indeed, this study initially originated from an attempt to compute the vibrational modes of three dimensional clusters. In three dimensions, we were unable to reach the elastic limit for the larger sizes (10000 atoms) that could be investigated at the time.