Slow relaxation and aging phenomena at nano-scale in granular materials

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Complex systems having metastable elements often demonstrate nearly log-time relaxations and a kind of aging: repeated stimuli weaken the system’s relaxation response. Granular matter is known to exhibit a wealth of such behaviors, for which the role of thermal fluctuations is usually ignored. However, we demonstrate that the latter can pronouncedly affect contacting mesoscopic-scaleasperities and be macroscopically observed via appropriate acoustic effects. We also propose a mechanism comprising slow relaxations and aging as intrinsic properties of a wide class of systems with metastable states.

Introduction – Slow relaxation phenomena in granular systems attract much attention due to both high importance of granular materials for geophysics and many industries and due to general physical interest to behavior of complex, glassy-type systems for which granular materials act as macroscopic analogs of ensembles of individual atoms and molecules. In particular, slow compaction of granular materials due to mechanical perturbations has been widely studied and it has been shown that, in such a process, the response of the material is related to – sporadic – grain rearrangements. Compared to slow macroscopic (i.e. grain-scale) rearrangements in granular materials, processes on the mesoscopic level (i.e. below micrometer, down to nanoscale) driven by natural thermal fluctuations are much less studied. The latter are reasonably believed irrelevant to grain rearrangements during compaction and jamming-unjamming transitions, but using appropriate acoustic techniques, spontaneous thermally-activated mesoscopic-scale processes can also be quite macroscopically observed. In particular, observations of slow relaxation of the elastic-modulus value in laboratory samples with cemented granular structure as well as similar effects in field measurements in sandy soil on a scale of ~ 10 m are known. High-intensity acoustic “conditioning” or a mechanical impact perturbed weakest bonds and produced perturbations in the material elastic modulus of order 10⁻⁶ – 10⁻³ that were rather problematic to monitor. To overcome this difficulty, it is desirable to reveal a parameter that is dominated not by the stable material skeleton, but precisely by the perturbed weak-bond-network. To this end, we make use of an acoustic-signal component produced by the own material nonlinearity, which is strongly dominated by the contributions of the weakest-contact fraction. We show that aging of granular materials induced by mechanical perturbations can be explained through a physical mechanism, based on the bistable character of contacts.

Methods – Feasibility of this idea was demonstrated in [10] by using the so-called nonlinear cross-modulation technique to monitor structural perturbations in granular material bulk induced by weak mechanical shocks. Another, practically simpler, nonlinear-demodulation technique was successfully applied for studying fine structural changes – avalanche precursors – in slowly tilted granular packings. Here, the sounding technique combined with pulse-type perturbations like in [10] is used to study slow relaxation of the weak-bond network in granular material with particular attention to revealed aging of material undergoing repeated perturbations. The experimental system is a 1 mm or 2 mm glass bead packing in a container to which a small electromagnetic shaker is attached. It produces rather weak (comparing to typical conditions of tap-induced compaction) perturbing pulses. The strain amplitude of the perturbing waves is varied in different measurements from about 10⁻⁷ to 10⁻⁶ and their duration is of 20 ms. The primary AM-modulated wave is at strain amplitude ε ∼ 10⁻³ – 10⁻⁶. Unlike observations of the primary wave (used in [10]) dominated by the medium skeleton, we use the demodulated component that is strongly dominated by the weakest contacts in the material, because nonlinearity of the weakest, least-loaded Hertzian contacts strongly exceeds nonlinearity of stronger contacts forming the stable skeleton of the material.

Figure shows various examples of slow relaxation in granular materials, observed using their nonlinear-acoustic response. As a function of time, the latter demonstrates power-law rates close to 1/tⁿ⁺ε with |n| ≪ 1, i.e., close to log-time behavior corresponding to n = 0. Plots (a) and (c) demonstrate peculiar weakening of the material reaction to series of identical taps, i.e., a kind of “aging”. Plots (a) and (b) also show much higher sensitivity of the nonlinearity-produced signal to the state of broken and then gradually restored weakest bonds compared with the fundamental component variability. As
argued in [11], such rapid and strong drops in the demodulated signal are related to breaking of the weakest contacts. Their nonlinearity is significantly higher than that of stronger contacts composing the material skeleton and dominating its linear elastic moduli. Thus the post-shock signal increase reflects restoration of broken contacts. Note that even if the probing signal is switched off just after the shock and switched on after a pause, the nonlinearity restores spontaneously, showing that the probing wave influence does not dominate the effect, although high-intensity acoustic strains (say $10^{-5}$) may even be able to perturb the weak bonds as in [8, 13].

Mechanism – Under room temperature $T \sim 300$ K the characteristic thermal energy $k_B T$ ($k_B$ is the Boltzmann constant) unambiguously indicates that thermal fluctuations cannot affect the state of visible (even weakly loaded) macroscopic contacts usually considered [6, 7] in granular matter modeling. Thus only mesoscopic surface asperities (from tens to hundreds of nanometers) can be considered as candidates of bistable structural elements potentially sensitive to thermal fluctuations. To understand the origin of their bistability, the analogy with the bistable behavior of tips in atomic-force microscopy (AFM) is very useful. For a tip already compressed by the contacting solid, the elastic Hertzian force is repulsive, whereas the tip yet approaching a solid surface experiences the influence of short-range attraction forces (often modeled using the Lennard-Jones potential). This attraction force for a AFM tip approaching another solid is equilibrated by the elasticity of the cantilever (dashed lines in Fig. 2a). If the cantilever is soft enough, a bistability zone can appear [12] as illustrated in Fig. 2a. In this zone, for a given initial position $A_1 \leq A \leq A_2$ of the unstressed cantilever, it can equilibrate the attraction force at two positions of the tip, “closed” and “open”, (in the latter, the attraction force is almost absent). If the cantilever is moved forth and back, peculiar hysteretic jumps between the two positions occur (see arrows in Fig. 2a). Inside the bistability zone eventual perturbations (e.g., sufficiently strong thermal fluctuations) can cause transitions between the two equilibrium states.

At first glance, for mesoscopic asperities at grain surfaces, there is no “soft cantilever” to create bistable equilibria by analogy with AFM. However, one can recollect general arguments [15] leading to the fact that for compressed contacts (not necessarily ideally spherical), the stored elastic energy scales as $h^{5/2}$ (where $h$ is the displacement of the contact apex). This means that for a compressed contact, the elastic force $F_{\text{comp}}$ scales by the famous Hertzian law $F_{\text{comp}} \propto h^{3/2}$. But the same arguments applied to a contact apex displaced by the value $|h| = |x - A|$ due to a localized attractive (stretching) force also lead to appearance of a tensile elastic force $F_{\text{tens}} \propto |x - A|^{3/2}$ that equilibrates the attraction (see dash-dotted curves in Fig. 2b).

Unlike AFM cantilever elasticity, this elastic force is nonlinear, i.e., initially it can be sufficiently soft to cre-
with glass-like materials, one concludes that for contacts but without the necessity of an artificial soft cantilever).

Teresis) to JKR-model for larger contacts exhibiting adhesion hysteresis to JKR-model for larger contacts exhibiting adhesion hysteresis (compare the curves for \( r = 30 \) nm and \( r = 200 \) nm and other identical parameters in Fig 2(b)). Thus, bistable equilibria with two-minima potential wells can appear in a finite range of separations between the asperity tip and the opposite surface without a real soft cantilever. Fig. 2(c) schematically shows how the resulting two-minima potential evolves with the initial separation \( A \). These representations suggest physically clear interpretation to the well-known [8] transition from the so-called DMT-model of very small contacts (that do not exhibit adhesion hysteresis) to JKR-model for larger contacts exhibiting adhesion hysteresis. The latter can be viewed as a special case of mechanical hysteresis (much like for AFM tips, but without the necessity of an artificial soft cantilever).

Assuming elastic and surface energy constants typical of glass-like materials, one concludes that for contacts with \( r \sim 10^2 \) nm and room temperature \( T \sim 300 K \), there are narrow regions near the boundaries of the bistability zone, where one of the potential wells \( E_b \) or \( E_c \) (Fig. 2b) is much greater than \( k_B T \) (say \( 10^2 - 10^4 \) times), whereas the other one is \( \sim 10^1 k_B T \) (see Fig. 2d for \( r = 100 \) nm). Thus, near the left boundary of the bistability region the closed state is much stabler, whereas the open one is metastable. Near the right boundary, the situation is opposite. The metastable equilibrium energy is comparable with that of thermal fluctuations, so that the latter are able to induce jumps to the opposite stabler state with characteristic waiting times \( \tau \exp(E_{b,c}/k_B T) \) according to the Arrhenius law, where the attempt time \( \tau_0 \) for nanometer-scale tips of the asperities can reasonably be taken \( \tau_0 \sim 10^{-12} s \).

Direct AFM inspection of the glass-bead surfaces confirmed the presence of numerous asperities about \( 10^2 \) nm in radius and 20–50 nm in height (Fig. 3a) consistent with the values reported in [19]. A single contact between two grains leads to \( 10^3 - 10^4 \) micro-asperities. Even if 1% of them actually gets in contact, one obtains \( \sim 10^2 \) of such mesoscopic contacts for a visible one. Following [11] we conclude that contribution of such loose but numerous micro-contacts can dominate over the nonlinearity of much stronger (and thus less nonlinear) macro-contacts creating the material skeleton. This explains why nonlinearity can drop drastically after fairly weak perturbations that still leave the material skeleton intact, but can suffice to break the mesoscopic contacts.

Figure 3b shows the physical meaning of relaxation of the number of closed mesoscopic contacts (left) and populations \( N_b(E) \) of broken ones (right). Labels 1 are for the initial state of just prepared packing with \( N_b(E) = 1 \) relaxed during 30 s ((a) and (b)) and during 1500 s ((c) and (d)). Labels 2 are for the system state just after a fairly weak perturbing shock that breaks only a portion of earlier closed contacts. Labels 3 correspond to the system states 24s after the shock. Compare experimental Fig. 1d with Fig. 4a, where the dashed curve shows continuous relaxation.
Kinetic Monte Carlo – We simulated the above discussed transitions between “open” and “closed” contacts (their total number in simulations is $3 \cdot 10^4$) using a kinetic Monte-Carlo approach. It uses Arrhenius transition probabilities characterized by the energy barriers $E_{bc}$ for jumps into closed states and $E_b$ to broken states. To match experimental time scale we restrict ourselves to $0 \leq E_{bc} \lesssim 45k_BT$. If initially all mesoscopic contacts are broken, the population of closed contacts is zero, $N_b(E) = 0$, whereas the broken states are fully populated, $N_b(E) = 1$. Gradual closing (relaxation) of the broken contacts looks as the motion of the “closing front” of $N_b(E)$ from small energy barriers to larger ones towards the right boundary of the bistability zone (as shown in Fig. 4b and 4d, curves 1, for two moments 30s and 1500s). The rate of the front motion exponentially decreases with time. We recall that the energy scale of the abscissa is proportional to distances from the bistability-zone boundaries. This means that tensile perturbations temporally shift the micro-contacts (including those corresponding to the current position of the “relaxation front”) towards the right boundary of the energy diagram. There, the energy wells for the open states are deep, whereas those for closed states are shallow (see Figs. 2c and 3b), so that transitions of previously closed contacts back to open states are fostered.

As a result, the pre-shock position of the closing front (Fig. 4b,d, curves 1) by the ending of the shock becomes shifted back to the left (Fig. 4b,d, curves 2), but then the closing front continues its movement to the right. For the same shock amplitude and duration, the resulting amount of the broken contacts that increase the population $N_b(E)$ essentially depends on the position of the closing front just before the shock. Notice the much smaller difference between curves 2 and 1 (Figs. 4b and 4d) for the initial relaxation time 30s than for 1500s. Sufficiently strong perturbations simply shift all bistable contacts to the right beyond the bistability zone (where only open states exist) and break all earlier closed contacts. Since displacements of contacts in granular materials for grains of radius $R$ can be estimated as $\varepsilon R$ for mechanical strain $\varepsilon$ and since the width of the bistability zone is of the order of an atomic size, such “strong” shocks correspond to strains $\gtrsim 10^{-6} - 10^{-5}$ for millimetric grains. For weaker shocks, the system response can be rather non-trivial and multi-variant depending on shock amplitude, duration, and previous history, e.g., the number of previous shocks and inter-shock intervals. For example, besides the difference in perturbation strengths, Fig. 4 shows that for the same post-shock relaxation time, the closing front 3 gets already to the right from its initial position 1 in panel 4b in contrast to the opposite situation in panel 4d.

Next, it should be recalled that besides the difference in the barrier energies $E_{bc}$ the widths of bistability regions can strongly differ for different-size contacts. Thus, the same perturbation can be “strong” for smaller contacts and “weak” for larger ones (as defined above), so that perturbation/relaxation regimes for such fractions of bistable elements are quite different. Similar situations can occur, e.g., for magnetic domains and other mesoscopic structural units that are not identical unlike individual atoms (molecules) of the same type.

For the above-discussed features, the “aging” of relaxation response to fairly weak perturbations is a natural consequence. Namely, a series of periodical moderate-strength shocks applied to previously well-relaxed material (Fig. 4c and d) gradually shifts the system state towards the one shown in Fig. 4a and b. Nevertheless, the regime shown in Fig. 4a and b (for which the relaxed front 3 lies to right from the initial position 1) is not reached, because the system response saturates when the relaxation between the shocks becomes able to heal the perturbation $\Delta N_b$ produced by every previous shock. This saturated value $\Delta N_b$ caused by repeated weak perturbing action of a fixed amplitude becomes significantly smaller than the reaction $\Delta N_b$ of the well-relaxed system to the initial shocks. The transition to such “aged” reaction of the system is shown in Fig. 5 for the simplest situation of identical mesoscopic contacts for which the barriers differ only due to different initial separations $A$). This model already fairly well reproduces the experimentally observed (see Fig. 1c) gradual “aging” of the system response to repeated weak shocks.

The discussed mechanism of micro-contact destruction/restoration does not necessarily imply impact-like perturbations. It is directly relevant to the observations of avalanche precursors in slowly tilted granular packings that can be viewed as internal “shocks”, after which the relaxation is also due to the discussed mechanism. Furthermore, sufficiently gentle tilt-induced strain variations can also cause slow breaking of the mesoscopic contacts as shown in Fig. 1b. If the critical angle is not reached and forth-and-back tilts are periodically repeated (with $\sim 1$ min. period), tilt-induced variations...
in the demodulated-signal amplitude strongly decrease (become "aged"). However, if the system is again tilted after \(\sim 1\) hour rest (during which the broken mesoscopic contacts spontaneously restore), the excursion of the signal variations also significantly restore (see [12]). Very high sensitivity of this technique is related to the fact that atomic-scale (and even sub-atomic) displacements control the observed nonlinear-acoustic response.

In the above discussion of the nonlinear-acoustic response determined by cumulated contribution of large contact ensembles we focused on weak perturbations, after which the relaxation of the ensemble was considered as an independent act for each mesoscopic contact. However, estimates show that if a significant portion of such contacts is broken, the surfaces of the macroscopic inter-granular contacts can experience atomic scale separation (comparable with or even greater than individual bistability-zone widths). This means that for stronger perturbations, the jumps of mesoscopic contacts between the bistable equilibria are not independent, and important role should be played by the secondary, really collective hysteretic/relaxational mechanisms that will be discussed elsewhere. Nevertheless, even for the small-perturbation regime, the revealed mechanism of independent nearly-logarithmic (or power-law) relaxations ensures a rich variety of possible regimes. In particular, the aging effect has a rather general nature and should manifest itself for a wide variety of complex systems containing large ensembles of relaxing mesoscopic units.

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