Toward Bernal Random Loose Packing through freeze-thaw cycling

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How a large number of solid objects can fill a volume is one of the most puzzling problems in mathematics, science and engineering. This question concerns a broad range of systems: granular media, colloids, structures of living cells, amorphous solids, . . . The relevant parameter that characterizes a pile of particles is the dimensionless packing fraction \( \eta \), defined as the volume of all particles divided by the apparent volume of the assembly. This packing fraction has a maximum value \( \eta_{\text{ter}} = 0.595 \) independently of its initial value \( \eta_0 \). This behavior is well reproduced by numerical simulations. Moreover, the numerical results allow to analyze the packing structural configuration.

With a Voronoi partition analysis, we show that the piles are fully random during the whole process and are characterized by two parameters: the average Voronoi volume \( \mu_v \) (related to the packing fraction \( \eta \)) and the standard deviation \( \sigma_v \) of Voronoi volumes. The freeze-thaw driving modify the volume standard deviation \( \sigma_v \) to converge to a particular disordered state with a packing fraction corresponding to the Random Loose Packing fraction \( \eta_{\text{RLP}} \) obtained by Bernal during his pioneering experimental work. Therefore, freeze-thaw cycling is found to be a soft and spatially homogeneous driving method for disordered granular materials.

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We study the effect of freeze-thaw cycling on the packing fraction of equal spheres immersed in water. The water located between the grains experiences a dilatation during freezing and a contraction during melting. After several cycles, the packing fraction converges to a particular value \( \eta_{\text{RLP}} = 0.595 \) independently of its initial value \( \eta_0 \). This behavior is well reproduced by numerical simulations. Moreover, the numerical results allow to analyze the packing structural configuration. With a Voronoi partition analysis, we show that the piles are fully random during the whole process and are characterized by two parameters: the average Voronoi volume \( \mu_v \) (related to the packing fraction \( \eta \)) and the standard deviation \( \sigma_v \) of Voronoi volumes. The freeze-thaw driving modify the volume standard deviation \( \sigma_v \) to converge to a particular disordered state with a packing fraction corresponding to the Random Loose Packing fraction \( \eta_{\text{RLP}} \) obtained by Bernal during his pioneering experimental work. Therefore, freeze-thaw cycling is found to be a soft and spatially homogeneous driving method for disordered granular materials.

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In the present letter, we show how the packing fraction of a spheres pile totally immersed in water is modified by successive freeze-thaw transitions. Moreover, the evolution of the packing structure during freeze-thaw transitions have been analyzed with Voronoi partition method applied on packings obtained by numerical simulations.

A sketch of the experimental set-up is presented in Figure [1]. A borosilicate glass tube of internal diameter \( D_{\text{tube}} = 18.4 \) mm is filled with water. Afterward, a granular material made of glass spheres with a diameter \( D_{\text{grain}} = 0.5 \) mm is poured gently inside the tube. This method leads to a loose initial packing fraction. To obtain a higher value of the initial packing fraction, the tube is placed inside an ultrasonic cleaning tank during one minute. The vibrations induce a compaction of the granular bed. To perform temperature cycling, the tube is placed inside an isotherm box. The temperature is
decreased with a Peltier module. The temperature increase is produced by a resistive wire winded around the glass tube. Two thermocouples measured respectively the temperature of the air inside the box and the temperature inside the granular material. A CCD camera takes pictures of the top of the granular pile. The position of the water meniscus is also visible on the pictures. The height of both water/air and granular/water interfaces are obtained by image treatment. Test runs with no thermal cycling were performed to ensure that vibrations do not affect the measurements. Moreover, thermal cycling have been performed on granular pile without water. In this dry case, we do not observe any significative variation of the packing fraction with our experimental set-up.

The volume thermal expansion coefficient of the glass beads and of the tube are respectively \( \beta_{\text{glass}} = 25.5 \ \mu K^{-1} \) and \( \beta_{\text{voro, glass}} = 9.9 \ \mu K^{-1} \). The water thermal expansion coefficient varies significantly with the temperature and ranges between \(-50 \ \mu K^{-1}\) to \(207 \ \mu K^{-1}\) when the temperature goes from \(1^\circ\text{C}\) to \(20^\circ\text{C}\). A rough estimation of the different material expansion for a temperature ramp between \(0^\circ\text{C}\) and \(20^\circ\text{C}\) gives \(0.02\%\) for the tube, \(0.05\%\) for the grains and \(0.15\%\) for the water. Moreover, during the freezing transition, the water volume increase is around \(8\%\). These estimations show that the presence of water in the system is expected to influence deeply the thermal cycling compaction dynamics, in particular during freeze-thaw transitions.

The pile is submitted to freeze-thaw cycling with temperature ranging from \(T_1 = -4^\circ\text{C}\) and \(T_2 = 24^\circ\text{C}\) (see Figure 2 (bottom)). The pile temperature reaches negative values before freezing. Therefore, a supercooling effect is observed. The time necessary to obtain a freezing of the system fluctuates from one cycle to the other. During the freezing transition, the temperature inside the pile goes quickly to \(0^\circ\text{C}\). During this fast freezing step, the position of the granular/liquid and liquid/air interfaces do not change significantly (see Figure 2 (Top)). However, during the temperature decrease after this freezing transition, both interfaces are going up. Then, a dilatation of the whole system is observed. Some steps are observed during this increase. When the pile temperature reaches \(T_1 = -4^\circ\text{C}\), the Peltier module is switched off and the heating is powered on. As a consequence, the temperature inside the pile increases to the temperature \(T_2 = 24^\circ\text{C}\) with a plateau at \(0^\circ\text{C}\). During the heating, the interfaces are going down. Some steps are also observed during this heating process.

The evolution of the packing fraction \(\eta\) as a function of the cycle number \(n\) is presented in Figure 2 (top). Three experiments performed with different values of the initial packing fraction \(\eta_0\) are presented. The experimental data are well fitted by the single exponential law proposed by Mehta et al.\[24\] \(\eta(n) = \eta_\infty - \Delta\eta e^{-n/\tau}\), where \(\eta_\infty\), \(\Delta\eta\) and \(\tau\) are respectively the asymptotic packing fraction, the range of packing fractions and a characteristic cycle number. For low initial packing fraction, the freeze-thaw cycling induces a densification of the pile \((\eta_\infty = 0.592 \pm 0.001, \Delta\eta = 0.019 \pm 0.001\) and \(\tau = 3.5 \pm 0.3\)\). On the other hand, a decompaction is observed for higher initial packing fraction \((\eta_\infty = 0.596 \pm 0.002, \Delta\eta = -0.021 \pm 0.001\) and \(\tau = 3.4 \pm 0.7\)\). In both case, the packing fraction is found to converge to the Bernal Random Loose
Packing fraction $\eta_{\text{BRLP}} = 0.60$. Moreover, the packing fraction is not influenced by freeze-thaw cycling when the initial packing fraction is close to $\eta_{\text{BRLP}}$. Therefore, this particular packing fraction should correspond to a specific structural configuration of the packing.

Although the compaction was expected for a loose initial packing fraction, the decompaction process of a dense pile is surprising. Moreover, the convergence of the packing fraction to the Bernal Random Loose Packing fraction $\eta_{\text{BRLP}} = 0.60$ is striking. In order to analyze the structural evolution of the packing during freeze-thaw cycling, numerical simulations have been performed. The model is based on molecular dynamics with tangential spring in order to produce a static pile. To obtain details about the numerical method, see ref [28]. A tube of diameter $D_{\text{tube}} = 10\text{mm}$ is filled with $N=1850$ grains of diameter $D_{\text{grain}} = 1\text{mm}$. The grains have the density of glass ($\rho = 2500 \text{ kg m}^{-3}$). After the initialization method, the voids between the grains are filled with spheres having the density of water. The void positions are obtained by Voronoï tessellation. Typically, 8000 void spheres are added. A freezing step consists in the dilatation of the void spheres, while a thaw step corresponds to a contraction of the void spheres. The evolution of the pile during a simulated freeze-thaw cycle is presented in Figure 4. When two void spheres are overlapping, a spring link is defined between them in order to avoid collapse during the dilatation process. As shown by Figure 4 (bottom), the compaction for loose initial packing fraction ($\eta_{\infty} = 0.594 \pm 0.001$, $\Delta \eta = 0.019 \pm 0.001$ and $\tau = 9.7 \pm 1.2$) and the decompaction for higher initial packing fraction ($\eta_{\infty} = 0.600 \pm 0.001$, $\Delta \eta = -0.005 \pm 0.001$ and $\tau = 5.0 \pm 0.5$) are well reproduced by the simulations. The characteristic cycle number obtained in simulations and in experiments are different because the size of the grains and of the container are different in experiments and in simulations.

The packings obtained by numerical simulations have been analyzed with Voronoï partition. The probability density functions of the Voronoï cell volumes $V$ for all the initial piles and for all the piles after 20 freeze-thaw cycling are presented in Figure 5. The volume normalization $(V - \mu_{V})/\sigma_{V}$ with the Voronoï volume average $\mu_{V}$ and the Voronoï volume standard deviation $\sigma_{V}$ induces a collapsing of the density functions. Then, the volume average $\mu_{V}$ and the volume standard deviation $\sigma_{V}$ are the main parameters characterizing the system. The volume average $\mu_{V}$ is related to the packing fraction $\eta = V_{\text{grain}}/\mu_{V}$, where $V_{\text{grain}}$ is the volume of one grain. Moreover, the Gamma shape of the density functions is characteristic of a fully random system [29]. We have tested with numerical simulations that an other driving mechanism like vibrations induces a deviation from the Gamma shape due to the apparition of ordered domains. Therefore, freeze thaw cycling is found to be a soft driving method for disordered granular materials. The driving modify the volume standard deviation $\sigma_{V}$ to converge to a particular disordered state with a packing fraction close to $\eta_{\text{BRLP}} = 0.60$. Contrary to driving processes based on mechanical agitation, we do not observe any convective motions, any grains spatial organization in the bulk and any grains ordering close to the container wall [11][13]. Moreover, the driving method based on freeze-thaw cycling is spatially homogenous.

A diagram with the main parameters obtained from the simulated packings (packing fraction $\eta = V_{\text{grain}}/\mu_{V}$ to consider
and standard deviation $\sigma_v$ of the Voronoi volumes) is presented in Figure 6. Aste et al. [6] have shown that $\sigma_v$ decreases between the random loose and the random close packing limits. Moreover, they observed a small but sizable local minimum around $\eta = 0.60$. This behavior was observed with experimental and numerical granular assemblies created in different conditions. The freeze-thaw cycling allow to move in this diagram along the master curve describe by Aste et al. We have checked numerically that a stronger mechanical driving mechanism like vibrations induces a deviation from this master curve due to the apparition of ordered clusters in the packing and close to the wall.

In summary, the evolution of the packing fraction of an assembly of spheres immersed in water and submitted to freeze-thaw cycling has been investigated. As already observed in the dry case, the packing fraction increases when starting from a loose configuration. However, when starting from a close configuration, the freeze-thaw cycling induces a decompaction of the pile. Independently of the initial packing fraction $\eta_0$, the packing fraction converges to a particular value $\eta_\infty = 0.595$. This final packing fraction is equivalent to the Random Close Packing fraction obtained by Bernal during his precursor experimental works performed in the sixties. Contrary to driving processes based on mechanical agitation, we do not observe any convective motions, any grains spatial organization in the bulk and any grains ordering close to the container wall. In addition, the driving based on freeze-thaw cycling is spatially homogenous. A structural analysis based on Voronoi partition has been performed with numerical simulations. The distribution of the Voronoi has shown that the packings are fully random during the whole process. Moreover, the packing fraction $\eta = V_{\text{grain}}/V_\mu$ and the Voronoi volume standard deviation $\sigma_v$ are the main parameters characterizing the piles.

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