When a suspension freezes, a compacted particle layer builds up at the solidification front with noticeable implications on the freezing process. In a directional solidification experiment of monodisperse suspensions in thin samples, we evidence a link between the thickness of this layer and the sample depth. We attribute it to an inhomogeneity of particle density induced by the sample plates. A mechanical model enables us to relate it to the layer thickness with a dependency on the sample depth and to select the distribution of particle density that yields the best fit to our data. These results clarify the implications of boundaries on suspension freezing. They may be useful to model polydisperse suspensions since large particles could play the role of smooth boundaries with respect to small ones.

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I. INTRODUCTION

The solidification of suspensions is a phenomenon that appears both in nature and in dedicated applications. In nature, repeated freezing/thawing cycles induce frost heave [1-3], ice lens formation [4,5] or cryoturbation [6] whose implications on soils are responsible for costly damages to roads, buildings or manmade structures. Applications address food engineering [8], cryobiology [9-11] or the fabrication of materials to obtain particle-reinforced alloys [12] by casting or bio-inspired porous or composite materials by freezing [13]. The quest for understanding the mechanisms at work in these different processes has stimulated a number of studies dedicated to the interaction of single [14-21] or multiple particles [6,22-26] with a solidification front.

In particular, in a number of situations, the front velocity is too slow to trap an isolated particle. A compacted particle layer then develops ahead of the front until trapping conditions are eventually reached [23,25,26] and make the layer stop growing. The mechanical features, the organization and the interaction of this layer with the solidification front are essential to predict or uncover the global evolution of a freezing suspension. However, suspensions are usually considered in an unlimited space whereas some degree of confinement may be present in practice due to system boundaries or to inclusions of additional elements of large size compared to particles (e.g. gravels or rocks). Considering the influence of space confinement on suspension solidification may thus provide valuable information for material processing or for modeling the freezing of composite suspensions. We address this issue here by using the availability of varying the suspension depth that is offered by the directional solidification of suspensions in thin samples.

Changing the depth of the samples in which the directional freezing of monodisperse suspensions is studied, we evidence, at any solidification velocity, a variation of the particle layer thickness with the sample depth. On the other hand, observation of particles close to the sample plates reveals an hexagonal lattice configuration that differs from the expected random close packing far away. This results in a variation of particle volume fraction along the sample depth whose implication on the particle layer thickness is determined using a mechanical model. Considering different relevant models of layer inhomogeneity enables a confrontation to the experimental data and the selection of the best fitting particle density evolution. This yields us to recover the layer thickness evolution with the sample depth and to refine the determination of the mean thermomolecular pressure exerted by a particle layer on particles nearing the front. It should be a priori possible to extend these determinations to any particle size and any suspension.

Section II describes the experiment setup and the generic evolution with the solidification velocity of the particle layer thickness. Section III first establishes the link between this evolution and the repelling thermomolecular pressure exerted by the solidification front on nearby particles. It then reports the different evolutions measured for various sample depths. Section IV addresses the origin of the inhomogeneity of particle density in the particle layer and its mechanical implication on trapping particles. Several models of particle density are then considered to recover the experimental variations with sample depth. A discussion and a conclusion about the study follow.
II. EXPERIMENT

A. Setup

The experimental setup aims at achieving the directional solidification of a thin sample under controlled conditions while allowing the visualization of the vicinity of the solidification interface. It was originally conceived for the directional solidification of binary mixtures [27-29] It consists in pushing at a definite velocity a sample in a uniform thermal gradient [Fig. 1(a)].

The sample translation is obtained from a screw rotated at a controlled rate by a microstepper motor. Thanks to a recirculating ball screw, this rotation induces a regular translation of a sample holder on a linear track. With 6400 microsteps by turn and a 5mm screw pitch, the elementary displacement is 0.8µm. Vibration at the end of micro-displacements are minimized by the use of Foucault current to slow down the motor rotation. Velocities up to 50 µm.s⁻¹ can be achieved with relative modulations less than 3%.

A controlled thermal gradient is provided by heaters and coolers separated by a 10 mm gap. They are electronically regulated at temperatures ±20°C. As these temperatures place the melting isotherm in the center of the gap, the visualization of the solidification interface is facilitated and the thermal gradient dependence on the sample velocity V is minimized [27-30]. Both heaters and coolers involve copper blocks either heated by resistive sheets or cooled by Peltier devices. To ensure a good thermal contact and the absence of inclined thermal gradient, the samples are sandwiched by top and bottom thermal blocks. An external circulation of a cryogenic fluid at -30°C enables heat to be extracted from the Peltier devices and from the lateral sides of the setup. The whole setup is finally surrounded by insulating polystyrene walls to provide a closed dry atmosphere that helps avoiding condensation and ice formation.

Samples are composed of two glass plates separated by calibrated propylene spacers [Fig. 1(b)]. When held together, they delimit a parallelepipedic space in which the suspension is introduced by capillarity prior to sealing. The plates dimensions, 100×45×0.7mm³ for the top glass and 150×50×0.8mm³ for the bottom glass, have been chosen large enough for providing a large central zone free of boundary disturbances. The spacer thickness allows a variety of sample depth e. Here, five depths were studied : 16, 50, 75, 100 and 125µm.

The suspensions contained monodisperse polystyrene spheres of 3 µm diameter and density 1.03 at volume fraction φ₀ = 10% or 20%. They were manufactured by Mag- sphere Inc. and were stable over months. Their monodispersity has been confirmed by confocal microscopy. Solu- tal effects were investigated by filtering out the particles using chromatography micro-filters and looking for the morphological instability of planar solidification fronts in the resulting mixture. The large critical velocity then found, of several µm.s⁻¹, indicates a low concentration of additive. The dynamical viscosity µ of the liquid contained in the suspension was taken as that of water : µ = 1.8 × 10⁻³ Pa.s.

An optical access in the middle of the gap between heaters and coolers enable visualization of the vicinity of the solidification interface [Fig. 1(a)]. As particles diffuse light, observation may be achieved in either reflection or transmission (Fig. 2). In both cases, the intensity received depends on the particle volume fraction φ : low (resp. large) at large φ in transmission (resp. reflection). Whereas both methods provided grey images on both the solid and liquid phases due to their moderate particle volume fraction (φ₀ = 10% or 20%), the particle layer that forms in between at a much larger volume fraction (φ ≈ 0.64) appeared either dark (transmission) or bright (reflection). Interestingly, its apparent thickness remains the same whatever the optical method (Fig. 2). Both of them could thus be used to document the particle layer thickness in the vicinity of plates by reflection or through the entire sample depth by transmission. The former method was the most applied in the present study. In complement, confocal microscopy (Leica SP8, combined to a Leica DM6000 optical microscope), used with long working distance non-immersive objective (Leica HC PL APO 20x/0.70 CS) has also been used to determine the particle arrangement in the vicinity of the sample plates.

The directions of the solidification front, the sample depth and the thermal gradient will be taken as the x-axis, the y-axis and the z-axis respectively [Fig. 1(b)]. In particular, we note that the particle layer develops in the direction z, normal to the direction y of the sample depth.

B. Particle layer thickness

When a sample starts solidifying, particles are repelled by the solidification front. They then accumulate ahead of it in a particle layer which involves a large particle volume fraction φ (Fig. 3). The raising rate of its thickness is related, by particle conservation, to its mean volume fraction φ₀. In this setup, we found it to be close to the random close packing density in three dimensions φ₃ = 0.634 : φ₁ ≈ φ₃ [26]. This means that the build-up layer is compacted.

The occurrence of a compacted layer largely increases the hydrodynamic viscous dissipation in it and then, for reasons detailed in section IV B, the constraints pushing particles adjacent to the front to be trapped. At some value h of the particle layer thickness, particles are then no longer repelled but trapped by the solidification front. The particle layer thus ceases to grow so that h stands as its steady state thickness after the initial growth transient [23] (Fig. 3). Its value, of the order of a millimeter, displays the specificity of being both mesoscopic and related to the microscopic trapping mechanism of particles by the front. This makes h a variable both easy to mea-
depth and the thermal gradient respectively. The axes of the study to it.

ping mechanism. We shall thus dedicate the remaining method.

interestingly, it keeps the same thickness whatever the optical contrast, the intermediate zone turns from bright to dark. In-

change of optical methods inverses bright and dark zones. In

and an intermediate zone (the compacted particle layer). The

top zone (the liquid phase), a bottom zone (the frozen phase)

to viscous dissipation, the relevant flow velocity is that

h

differences [Fig. 4(a)]. This may be attributed to a wrong
discoveries regarding the particle volume fraction \( \phi_0 \) when the
to viscous dissipation. In particular, their difference correspond to a volume flux of liquid \( U \) with respect to the particle matrix equal to \( U = (1 - \phi_l)(v_l - v_p) \) or :

\[
U = -V(\phi_l - \phi_0) / \phi_l
\]

(Fig. 3). Whereas these velocities are equal in the incoming suspension, they differ in the particle layer, which

generates viscous dissipation. In particular, their difference should therefore be more relevant to refer to the particle layer thickness \( h \). This is apparent in figure 4(b) where the same data no longer display differences regarding the particle volume fraction \( \phi_0 \).

The graph \( h(1/|U|) \) displays a linear part up to \( 1/|U| \) \( < 1 \text{s} \cdot \mu \text{m}^{-1} \) followed by much slower increase [Fig. 4(b)]. We shall show in a forthcoming paper that the change of regime corresponds to the occurrence of a noticeable additional dissipation induced by solid friction at the sample plates. Here, we shall restrict to the linear trend which will be proved to be related to fluid viscous dissipation only. It stands for large enough velocities, i.e., \( U \) larger than a micron per second, and corresponds to \( h \propto U^{-1} \). This exponent differs from the exponent \(-0.72 \) reported by Anderson and Worster for alumina suspensions [25]. This difference may be due to the polydispersity of the alumina suspension or to the closeness to the transition to an ice lens regime where \( h \) is no longer steady.

In the remaining of the paper, we shall restrict attention to the large velocity regime in which \( h \) linearly evolves with \( 1/U \). We shall in particular focus attention on the way this linear relationship depends on the suspension depth \( e \).

### III. PARTICLE TRAPPING AND THERMOMOLECULAR PRESSURE

The trapping of a particle by a solidification front is a phenomenon which obviously involves the interaction between both of them, at a small scale. However, we shall see that the remaining particles of the layer, and hence, the whole particle matrix, also participate to it. This
offers the opportunity to indirectly measure the repelling thermomolecular force between particles and front, from the particle layer thickness $h$.

A. Force balance model

Three kinds of forces apply on a particle nearing a solidification front (Fig. 6):

i) The thermomolecular force $F_T$ exerted by the solidification front on an entering particle. It results from van der Waals and electrostatic interactions between the particle and the front and stands here as a repelling force. On an elementary particle surface, it corresponds to a normal force whose intensity quickly decreases with its distance to the front, as its inverse cube for non-retarded van der Waals interactions \[31,32 \] and as an exponential for electrostatic interactions \[31,33 \].

On a spherical particle, the resultant of this force is, by symmetry, normal to the particle base, or equivalently parallel to the thermal gradient direction $e_z$ (Fig. 6). Its intensity depends on the distance between the particle base and the front. However, as all particle layers stand in a state that corresponds to the repelling/trapping transition at the solidification front, we shall assume that this distance and thus the force intensity on a particle is a constant. This will be corroborated below by the linear variation of the layer thickness $h$ with the inverse velocity $1/U$.

An important implication of the thermomolecular force is to induce an additional pressure between particles and front which maintains a liquid phase between them, whatever the smallness of their distance \[22,34 \]. Flows can thus occur in these so-called premelted films, yielding a lubrication force.

ii) The lubrication force $F_L$ on an entering particle. It results from viscous effects in the thin premelted film that separates an entering particle from the solidification front (Fig. 6). Its resultant $F_L$ on a particle is by reason of symmetry parallel to the thermal gradient direction $e_z$. As the corresponding flows around the particle are creeping flows, the intensity of $F_L$ is linearly related to their magnitude and thus to the Darcy velocity $U : F_L = fU$, the prefactor $f$ depending on the geometry of the film that separates a particle from the front. However, in the large velocity regime studied here, the quantitative implication of the lubrication force will appear below to be negligible as compared to the force exerted by the particle layer on an entering particle.

iii) The force $F_\mu$ exerted by the particle layer on an entering particle.

It results from both the pressure drop and the viscous stresses induced by the fluid flowing across the particle matrix. It is transmitted to a particle nearing the front by contacts along the particle matrix.

The pressure gradient in the particle layer follows the Darcy law $\mu U = -k dP/dz$, where $\mu$ denotes the liquid viscosity, $k$ the medium permeability, $U$ the Darcy velocity and $P$ the fluid pressure. According to the Kozeny-Carman relation, the permeability $k(\phi_l, d)$ of the particle layer depends both on its particle volume fraction $\phi_l$ and on the particle diameter $d$:

$$k(\phi_l, d) = \frac{d^2}{180} \frac{(1-\phi_l)^3}{\phi_l^2}$$

A pressure drop $\Delta p = \mu U h/k$ is thus induced across the particle layer. This depletion of pressure at the solidification front is responsible on one hand for the cryosuction of liquid and on the other hand, for a pressure forcing the particles adjacent to the front to be trapped.

To compute it, we notice that a part $\phi_l \Delta p$ of the pressure drop is undergone by the particle matrix and a part $(1-\phi_l) \Delta p$ by the liquid phase. The latter part however corresponds to the rate of momentum flux on the direction $e_z$ that is lost by the fluid and gained by the particle matrix, due to viscous stresses on the particle surfaces. Altogether, the net constraint exerted by the liquid phase on the particle matrix, by both pressure and viscous stresses, thus amounts to $\Delta p$ on a unit surface of the suspension. However, as particles occupy only a part $\phi_l$ of a suspension section, the mean pressure on an entering particle reads $P_\mu = \Delta p/\phi_l$ or:

$$P_\mu = -|U| h \frac{\mu}{\phi_l k(\phi_l, d)}$$

As the particle layer stands in a critical state for trapping, its thickness and the resulting pressure $P_\mu$ have grown up to just reach a force balance on particles nearing the front. For convenience, we express it in terms of mean pressure rather than of forces, i.e. in terms of force component on $e_z$ divided by the particle section $\pi d^2/4$.

For particles adjacent to the front, the above analysis then yields $P_\mu + P_T = |fU|$ where $\mu \mu$, $P_L$ and $P_T$ denote the mean pressure exerted on an entering particle by the particle layer, the premelted film by lubrication and
FIG. 4: (Color online) Evolution of the compacted layer thickness $h$ with the solidification velocity. The sample depth is $e = 125\mu m$ and the particle volume fractions are $\phi_0 = 0.1$ and $0.2$. (a) Plot of thickness $h$ with respect to the inverse of the velocity $V$. (b) Plot of thickness $h$ with respect to the inverse of the Darcy velocity $U = -V(\phi - \phi_0)\phi$.

FIG. 5: Sketch of the system that shows the suspension, the compacted layer of particles and the frozen phase. The mean velocities of the fluid and of the particles with respect to the solidification front are denoted $v_f$ and $v_p$ respectively. In the suspension, they both equal the opposite of the solidification velocity. However, in the compacted layer of particles, they differ following the rise of particle volume fraction. As particles are randomly distributed, their section by a plane displays different radii although they actually have the same radius.

the solidification front by thermomolecular interactions. Among these pressures, two of them $P_{\mu}$ and $P_L$ tend to induce trapping and are therefore negative. In contrast, the remaining thermomolecular pressure $P_T$ tends to repel particles and is thus positive.

However, beyond a velocity $U_c$, the lubrication force is sufficient to induce particle trapping on a single particle. No particle layer can then build up since all particles coming on the front are trapped without delay. The force balance thus becomes : $P_L + P_T = 0$ with $P_L = gU_c$ and $g = f/\pi R^2$. This provides a link between the prefactor $g$ and $P_T$ which yields : $P_T = -P_L U/U_c$. Using the above determination of $P_{\mu}$, we then obtain the following relationship between the particle layer thickness $h$ and the thermomolecular pressure $P_T$ : 

$$h \frac{\mu}{\phi_0 k(\phi_1, d)} = P_T \left( \frac{1}{|U|} - \frac{1}{U_c} \right)$$

(4)

The occurrence in this relation of $U$ (which depends on $\phi_0$) instead of $V$ (which is independent of it) explains the convergence of data on a master curve in figure 4(b) when using the former. In addition, relation (4) provides an interesting connection between a macroscopic variable, $h$, and a microscopic one, $P_T$, that we shall exploit to evaluate the thermomolecular pressure $P_T$. 

FIG. 6: (Color online) Sketch of the forces acting on a particle entering the frozen phase: a thermomolecular repelling force $F_T$ exerted by the solidification front (black arrow); a lubrication force $F_l$ induced by the liquid flowing in the thin film which separates the particle and the front (red arrow); a force $F_{\mu}$ exerted by the particle layer on the particle, as a result of the viscous friction and the pressure drop induced by the liquid flow through the particle matrix (green dashed arrow). Blue curved arrows symbolize the liquid flow. The direction $e_z$, normal to the solidification front, is parallel to the thermal gradient. As particles are randomly distributed, their section by a plane displays different radii and few contact points here, although they actually have the same radius and are in contact with each other.
B. Thermomolecular pressure

Figure 7 reports for all the sample depths studied, the evolution of the layer thickness $h$ with the inverse velocity $|U|$, above $|U| = 1 \text{ m.s}^{-1}$. Following relation [4] and the fact that $\phi_l \approx \phi_3$, $h$ is multiplied by the normalization factor $\mu/\phi_3 k(\phi_3, d)$ so as to enable an easy connection with the thermomolecular pressure $P_T$. All graphs show a linear relationship whose slope provides an indirect measure of $P_T$ on a entering particle. All are statistically relevant except that performed at $e = 100\mu m$ which involves only three points. We nevertheless conserve it for completeness. The fact that data are well fitted by a linear relationship indicates that the critical velocity $U_c$ is large enough compared to velocity data for making its inverse negligible here. This means that, for all the situations studied, the pressure exerted by the particle matrix on an entering particle was far larger than the lubrication pressure on it, so that the force balance reduces to:

$$P_\mu + P_T = 0$$

Using $\phi_l \approx \phi_3$, the relation [4] then simplifies into:

$$h \frac{\mu}{\phi_3 k(\phi_3, d)} = \frac{P_T}{|U|}$$

As the thermomolecular pressure $P_T$ is set at the microscopic level across the thin premelted film that separates an entering particle from the front, one would expect it to be uncorrelated with macroscopic variables such as the sample dimensions. However, the above linear relationships show that their slopes, and hence the resulting determination of $P_T$, increase with the sample depth $e$. This is synthesized in figure 8 which gathers the best fitted linear relationships at various $e$.

This apparent dependence of the thermomolecular pressure $P_T$ on the sample depth $e$, $P_T \equiv P_T(e)$, thus seems somewhat paradoxical in the present framework since one would hardly understand a physical interplay between the small scale variable $P_T$ and the large scale dimension $e$. We shall show in the next section that the sample depth $e$ actually enters the picture, not on the thermomolecular pressure $P_T$, but on particle volume fraction $\phi_l$ of the layer.

IV. PARTICLE LAYER INHOMOGENEITY

The dependence of the layer thickness $h$ on the sample depth $e$ suggests an effect induced by boundaries, i.e., by the sample plates. It cannot be hydrodynamical since the compactness of the layer restricts the hydrodynamic boundary length to less than a particle diameter, a quantity too small to induce a global effect on the system. On the other hand, the flatness of the plates introduces a long-range correlation of position that can significantly affect the distribution of particles, and thus the physical features of the compacted layer. We address below this effect and its implication on the layer thickness.

A. Sample plate and particle ordering

In 1611, Kepler conjectured that the highest density of sphere packing in space, whatever the regular or irregular nature of its arrangement, was achieved with either an hexagonal close-packed or a face-centered cubic lattice. These lattices are made of superposed planar hexagonal arrangement [Fig. 9(a)] with different phases of superposition. In 1831, Gauss proved this conjecture in the restricted case of regular lattices. In the general case of arbitrary arrangements, it was finally proven by T. Hales 35 twenty years ago and later certified by a formal proof.

As these highest density arrangements of spheres are made of superposed planar lattices, they fit with a planar boundary. We shall thus call their density $\phi_2$ to state that it corresponds to the highest density achievable in a plane. It amounts to $\phi_2 = \pi/3\sqrt{2} \approx 0.74048$.

In contrast, when random arrangements of particles are considered instead of lattices, the highest possible density must be smaller. It has been found experimentally to be $\phi = 0.6366 \pm 0.0005$ 36 and has been shown to be at most 0.634 by statistical analysis of jammed states 37, although the concept of random arrangements may require clarification 38. We retain the latter determination for the highest density of random close packing. As it refers to sphere arrangements on the 3d space, we have called its density $\phi_3$.

Regarding the compacted layers of particles, as they are built by piling up incoming particles, one may expect them to correspond to the highest density compatible with this process. The specificity of a sample plate is then to force particles to be aligned on a plane in its vicinity, so that the highest density configuration then corresponds to hexagonal crystals. This is confirmed by confocal microscopy which reveals a particle arrangement at a sample plate made of hexagonal patches linked by crystalline defects [Fig. 9(b)]. The expected particle density is thus $\phi_2$ in the plate vicinity. Far from the plates, no large scale geometrical constraints are imposed to particles so that the packing should be random. Its highest density, $\phi_3$, is thus expected there and is actually close to the mean density measured during the layer build up 29.

Accordingly, the sample plates break the random close packing of particles and make it evolve towards a planar hexagonal arrangement close to them. This yields the particle density to raise from $\phi_3$ to $\phi_2$ when approaching these plates. We address below the mechanical implications of this layer heterogeneity and we propose some models of the transition of particle density from $\phi_2$ to $\phi_3$. 
FIG. 7: (Color online) Evolution of the thickness $h$ of the compacted layer with the inverse of the Darcy velocity $U$. For convenience, $h$ is multiplied by the factor $\mu/[\phi_0 k(\phi_3)]$ where $\phi_3$ denotes the particle volume fraction at random close packing. Sample depth: (a) $e = 16\,\mu\text{m}$. (b) $e = 30\,\mu\text{m}$. (c) $e = 50\,\mu\text{m}$. (d) $e = 75\,\mu\text{m}$. (e) $e = 100\,\mu\text{m}$. (f) $e = 125\,\mu\text{m}$. The particle diameter is $d = 3\,\mu\text{m}$.

B. Implication on the particle matrix pressure

From relations (1), (2), and (3), the pressure exerted by a particle matrix of density $\phi$ on particles nearing the front reads:

$$\bar{P}_\mu = -f(\phi, \phi_0)hV \quad (7)$$
with a dissipation factor $f$:

$$f(\phi, \phi_0) = \mu \frac{180 (\phi - \phi_0)}{d^2 (1 - \phi)^3}$$  \hfill (8)

From force balance, it yields a layer thickness inversely proportional to the dissipation factor $f$: $h = P_T / fV$. As $f$ increases with $\phi$, it is larger close to the sample plate than in the bulk of the compact layer. For a homogeneous thermomolecular pressure $P_T$, the inhomogeneity of the factor $f$ should yield a smaller layer thickness $h$ close to the sample plate than in the layer bulk. This is however denied by images of the compacted layer which show the same layer thickness by light transmission than by light reflection (Fig. 2). This indicates that the interplay between particles and fluids prevents the occurrence of columns of different heights in the compacted layer. Then, for an homogeneous thickness $h$ at a given velocity $V$, the inhomogeneity of volume fraction $\phi$ in the layer should a priori yield different pressures $P_\mu$ on particles nearing the front.

However, the stresses on the particle matrix tends to distribute homogeneously as described by the Janssen restitution coefficient [39, 40], whereas the fluid pressure tends also to equilibrate by fluid motion. We shall assume that the constraint exerted by the particle layer on the particles nearing the solidification front is homogeneous. We shall denote it $P_\mu^i$, the superscript recalling that it refers to an inhomogeneous distribution of particle volume fraction. We shall finally express it as the average of the constraints $P_\mu$ over the layer depth $e$:

$$P_\mu^i = -h V \frac{1}{e} \int_{-e/2}^{e/2} f(\phi, \phi_0) dy$$ \hfill (9)

with an origin of the $y$-axis placed in the middle of the layer depth [Fig. 1(b)] and a volume fraction $\phi$ a priori dependent on $y$: $\phi = \phi(y)$.

To make connection with the previous expression of $P_\mu$ [3] deduced for a homogeneous layer involving a particle volume fraction $\phi_1 \approx \phi_3$, we label it by a superscript $h$ and notice that:

$$P_\mu^i = \frac{1}{e} \int_{-e/2}^{e/2} f(\phi, \phi_0) dy \bar{P}_\mu^h$$ \hfill (10)

Following force balance [3], these pressures $P_\mu^h$, $P_\mu^i$, correspond to the opposite of the thermomolecular pressures relevant to homogeneous, $P_T^h$, or inhomogeneous, $P_T^i$, particle layers. Their relation (10) then translates to the thermomolecular pressures:

$$P_T^i = I \bar{P}_T^h$$ \hfill (11)

where $I[\phi(y), \phi_0, e]$ denotes the renormalization factor:

$$I = \frac{1}{e} \int_{-e/2}^{e/2} f(\phi, \phi_0) \bar{f}(\phi_3, \phi_0) dy$$ \hfill (12)

which conveys the effects of inhomogeneity.

As the trapping mechanism stands at the scale of a particle, one expects its onset to be independent of large scale situations. Accordingly, the thermomolecular pressure on entering particles should be homogeneous along the solidification front. However, assuming a uniform particle volume fraction $\phi = \phi_3$, we obtained a thermomolecular pressure $P_T^h = U h \mu / \phi k$ dependent on the layer thickness $e$: $P_T^h \equiv P_T^h(e)$ (Figs. 7 and 8). We guess that this dependency is an artifact induced by a particle layer inhomogeneity. Then, with a constant actual thermomolecular pressure $P_T^i$, the homogeneous estimate $\bar{P}_T^h = I^{-1} P_T^i$ [11] appears to depend on the sample depth $e$ via the renormalization factor $I[\phi(y), \phi_0, e]$.

Our objective will now be to uncover what suitable distribution of particle volume fraction $\phi(y)$ could recover this dependency and finally deduce the resulting actual thermomolecular pressure $P_T^i$.

### C. Volume fraction models

By symmetry, we expect an even distribution $\phi(y)$ of particle volume fraction with respect to the mid-plane $y = e/2$. This will enable us to restrain the computation of the inhomogeneity factor $I$ to a half layer. Then, for convenience, we change the origin of the $y$-axis and place it on the bottom plate. This way the plate location, $y = 0$, is fixed and that of the mid-layer, $y = e/2$, evolves with the layer thickness.

We shall first consider a sharp transition between hexagonal and random close packing and then an exponential relaxation between them. It will finally appear that a combination of both will be required to recover the variations observed with the sample depth $e$.
FIG. 9: (Color online) (a) Hexagonal close-packed lattice of spheres. This corresponds to the arrangement of spheres of highest density: \( \phi_2 = \pi/3\sqrt{3} \approx 0.74048 \). It is compatible with a planar boundary and is thus the highest density available at a sample plate. This density can prolongate away from the boundary with an hexagonal close-packed or a face-centered cubic lattice. (b) Confocal microscopy image of the compacted layer of particles close to a sample plate. The particle diameter is 3 \( \mu m \). The image shows large close-packed arrangements of particles with hexagonal order in a plane parallel to the plate. This implies a particle volume fraction close to \( \phi_2 \).

\[ \phi(y) \]

\[ \phi_2 \quad \phi_3 \]

\[ \text{Models} \]

- two layers
- exponential
- combined

\[ P_T^h \] (Pa)

\[ 0 \quad 1500 \]

\[ 0 \quad 20 \]

\[ 1184 \quad 1000 \]

\[ 500 \quad 0 \]

\[ 0 \quad 200 \]

\[ 15 \mu m \]

\[ 1463 \] Pa

FIG. 10: (Color online) Models and implications. (a) Models of the evolution \( \phi(y) \) of the particle volume fraction from the sample plate \( y = 0 \). (b) Best fits of the resulting evolution of the thermomolecular pressure \( P_T^h \) with the sample depth \( e \). Points correspond to the measures of \( P_T^h \) as provided by the slopes of figures 7 and 8. The green line indicates the asymptote of the combined model.

1. Two layers model

We consider the compacted half-layer as composed of two homogeneous sub-layers. One, of depth \( \delta \), is adjacent to the sample plate. It thus involves the highest particle density \( \phi_2 \). The other extends up to the mid-layer and involves random close packing with particle density \( \phi_3 \).

This model corresponds to a sharp transition between the limit densities \( \phi(0) = \phi_2 \) and \( \phi(\infty) = \phi_3 \):

\[ 0 \leq y \leq \delta : \phi(y) = \phi_2 \]
\[ \delta \leq y \leq e/2 : \phi(y) = \phi_3 \]

We label \( \alpha(\phi_0) = f(\phi_2, \phi_0)/f(\phi_3, \phi_0) \) the increase of dissipation factor \( f \) when changing the volume fraction from \( \phi_3 \) to \( \phi_2 \). Its values at \( \phi = 0.1 \) and \( \phi = 0.2 \) are close, respectively 3.378 and 3.508. We denote \( \alpha \) their average value 3.443 and, for simplicity, use it as representative of the two volume fractions studied.

We then obtain from (12) the inhomogeneity factor:

\[ 0 \leq e \leq 2\delta : I(\delta, e) = \alpha \]
\[ 2\delta \leq e : I(\delta, e) = 1 + (\alpha - 1)2\delta/e \]

The values of \( P_T^h(e) \) obtained from the slopes of figure 8 are reproduced on figure 10(b). The best fit of \( P_T^h(e) = I(\delta, e)^{-1}P_T^i \) with fitting parameters \( \delta \) and \( P_T^i \) yields \( \delta = 15.0 \mu m \) and \( P_T^i = 1463 \) Pa. The corresponding profiles of \( \phi(y) \) and of \( P_T^h(e) \) for this so-called two layers model are reported on figures 10(a) and (b).
The corresponding profiles of $\phi_{10}$ (a) and (b).

3. Combined model

Figure 11(b) reveals that the above models yield thermomolecular pressures $\bar{P}_{T}^{h}$ that increase with the sample depth, as determined experimentally. In particular, the two layers model recovers the stagnation of $\bar{P}_{T}^{h}$ at small $e$ and the exponential model reproduces the form of raise of $\bar{P}_{T}^{h}$ towards its asymptote. However, both are unable to fit the experimental data satisfactorily: the two layers model cannot follow the increase rate of $\bar{P}_{T}^{h}$ when the second layer develops; the exponential model cannot recover the stagnation of $\bar{P}_{T}^{h}$ at small $e$.

It thus appears that a mix of both models could be relevant. We then conserve an homogeneous layer at particle density $\phi_{2}$ close to the sample plate and prolongate it, beyond a distance $\delta$, by a smooth exponential relaxation towards the limit density $\phi_{3}$. The local volume fraction then reads:

$$0 \leq y \leq \delta : \phi(y) = \phi_{2}$$
$$\delta \leq y \leq \delta/2 : \phi(y) = \phi_{3} + (\phi_{2} - \phi_{3}) \exp(-y/\xi)$$

with $\delta$ the depth of the homogeneous ordered layer at the plate and $\xi$ the relaxation length of the particle density beyond.

The above analyses provide the variation with $e$ of the inhomogeneity factor $I(\delta, \xi, e)$:

$$0 \leq e \leq 2\delta : I(\delta, \xi, e) = \alpha$$
$$2\delta \leq e : I(\delta, \xi, e) \text{ as given by relation } \text{(14)}$$

with the above values of $\beta$ and $\gamma$ but $\epsilon = (\epsilon/2 - \delta)/\xi$.

The best fit of $\bar{P}_{T}^{h}(e) = I(\xi, e)^{-1} \bar{P}_{T}^{i}$ with fitting parameters $\delta$, $\xi$ and $\bar{P}_{T}^{i}$ yields $\delta = 22.4\mu m$, $\xi = 4.9\mu m$ and $\bar{P}_{T}^{i} = 1184$ Pa. The corresponding profiles of $\phi(y)$ and of $\bar{P}_{T}^{h}(e)$ for this so-called combined model are reported on figures 10(a) and (b). One obtains a satisfactory fit to the experimental data, both the stagnation at small $e$ and the raise towards the asymptote being well recovered by the best fit.

D. Renormalization of the thermomolecular pressure

The combined model thus satisfactorily recovers the data points $\bar{P}_{T}^{h}(e)$ with a best fitting value of the actual thermomolecular pressure $\bar{P}_{T}^{i}$ of 1184 Pa. It is however based on the guess that this thermomolecular pressure $\bar{P}_{T}^{i}$ is independent of the sample depth $e$. To check the consistency of our approach, we thus deduce a posteriori, at each sample depth $e$, the value of $\bar{P}_{T}^{i}(e)$ from the data of $\bar{P}_{T}^{h}(e)$, using relation (11) and the best fitting values $\delta = 22.4\mu m$ and $\xi = 4.9\mu m$ for $I(\delta, \xi, e)$. 

FIG. 11: (Color online) Renormalization of the thermomolecular pressure $\bar{P}_{T}$ on an entering particle following the combined model. Full circles : data $\bar{P}_{T}^{h}(e)$ determined for homogeneous layers. Full squares : data $\bar{P}_{T}^{i}(e)$ determined for inhomogeneous layers. Full line : best fitted value of $\bar{P}_{T}^{i}$ in the combined model of figure 10(b).

2. Exponential relaxation model

As a sharp transition between two packing densities is crude, we wish to model a continuous transition between them. We then consider an exponential relaxation of $\phi(y)$ from its value $\phi_{2}$ at the sample plate to the value $\phi_{3}$ far from it:

$$\phi(y) = \phi_{3} + (\phi_{2} - \phi_{3}) \exp(-y/\xi)$$

(13)

where $\xi$ denotes a relaxation length.

Standard integration from relations (12) and (13) yields the inhomogeneity factor $I(\xi, e)$:

$$I(\xi, e) = 1 + \frac{1}{\epsilon} \left\{ - \ln(1 - \beta) + (1 - \beta)^{-1} + \frac{\gamma}{2} (1 - \beta)^{-2} + \ln \left[ 1 - \beta \epsilon^{-\gamma} \right] - \left[ 1 - \beta \epsilon^{-\gamma} \right]^{-1} - \frac{\gamma}{2} \left[ 1 - \beta \epsilon^{-\gamma} \right]^{-2} \right\}$$

(14)

with:

$$\beta = \frac{\phi_{2} - \phi_{3}}{1 - \phi_{3}} ; \gamma = \frac{1 - \phi_{0}}{\phi_{3} - \phi_{0}} ; \epsilon = \frac{e}{2\xi}$$

(15)

The explicit values are $\beta = 0.292$, $\gamma = 1.685$ for $\phi_{0} = 0.1$ and $\gamma = 1.843$ for $\phi = 0.2$. Following the close values of $\gamma$, we adopt for simplicity its average value 1.764 for the two volume fractions studied. It agrees with the average value of $\alpha$ adopted above.

The best fit of $\bar{P}_{T}^{h}(e) = I(\xi, e)^{-1} \bar{P}_{T}^{i}$ with fitting parameters $\xi$ and $\bar{P}_{T}^{i}$ yields $\xi = 15.8\mu m$ and $\bar{P}_{T}^{i} = 1186$ Pa. The corresponding profiles of $\phi(y)$ and of $\bar{P}_{T}^{h}(e)$ for this so-called exponential model are reported on figures 10(a) and (b).
The renormalized values $P_T^i(e)$ of the thermomolecular pressure show in figure [11] a large constancy which contrasts with the large raise with $e$ of the estimation $P_T^h$ obtained by assuming a homogeneous layer. The best fitting value $P_T^i = 1184$ Pa then appears as a kind of average of the values determined for each sample depth $e$.

V. DISCUSSION

Varying the sample depth $e$ in our experiment led us to evidence, on compacted particle layers, the implications on their thickness $h$ of their inhomogeneity in particle density $\phi$. All these variables have been linked by a mechanical model of trapping in the multi-particle case where a compacted particle layer is in order. The evolution of $\phi$ that fits the best the data on $h$ consists in a stagnation from the sample plate at the highest possible value $\phi_2$ referring to an hexagonal close packing followed by an exponential relaxation towards the asymptotic value $\phi_3$ of random close packing.

Although these conclusions were obtained at a definite particle diameter, they are expected to extend to other particle sizes insofar as no other phenomena such as electrostatic interactions interfere. Accordingly, the quantitative determination of both the length $\delta$ of the sub-layer of density $\phi_2$ attached to the plate and the relaxation length $\xi$ towards $\phi_3$ beyond should better be considered in term of particle diameter $d$. This yields $\delta \approx 7.5d$ and $\xi \approx 1.6d$. Both provide a net influence length $\lambda = \delta + \xi$ of a smooth boundary on the particle density $\phi$ of $\lambda \approx 9d$. In comparison the two layers model and the exponential model both led a shorter influence length of $\lambda \approx 5d$. Their poor fitting of data as compared to the combined model shows the relevance of an influence length as large as $9d$ here. This agrees with the influence length of flat plates in granular flows which has been found to extend over at least $5d$ [11]. On the other hand, the small value of the relaxation length $\xi = 1.6d$ compared to the sub-layer length $\delta \approx 7.5d$ supports a sharp nature of the transition from $\phi_2$ to $\phi_3$. Direct analysis of the particle packing inside the suspension would be valuable to confirm this point.

On a general viewpoint, the transition from a random packing to an hexagonal packing when approaching the plate boundary corresponds to the formation of 2D colloidal crystals. While crystallization can spontaneously occur in colloidal suspensions [42], it has been found to be induced by shaking in granular materials [43]. In suspensions, this ordering may be encountered during evaporation or drying [44] or by hydrodynamic shear [45, 47]. It is then mediated by capillary forces or by shear stresses respectively. Here, particles are compacted and pressed on the sample plate by the pressure exerted by the particle matrix. This pressure seems necessary to induce crystallization since, on spheres packed by sedimentation in a fluidized bed, the particle density at the boundaries was smaller than in the bulk [48]. Here, this pressure raises from zero at its frontier with the liquid phase to the pressure $P_T$ at the solidification front. As it is weak in a part of the particle layer, it may thus not enough compress particles on the plates to reach the density $\phi_2$ there. We nevertheless assumed that this concerns a relatively negligible part of the layer.

Both the nature of random close packing and of the crystallization of sphere packing still raise open questions regarding the geometric frustration that prevents the former to cross the density limit $\phi_3$ and the particle rearrangements that enable crystal occurrence [49]. In particular, in random close packing, Bernal emphasized the relevance of local tetrahedral configurations yielding dense polytetrahedral aggregates [50]. These aggregates have indeed been related to geometric frustration and on crystallization, these issues still remain in debate. The present suspension indicates that, in presence of Darcy flows, the transition from random close packing to hexagonal crystal is sharp. Whether this is compatible with actual views on crystallization will be a stimulating issue to address.

The finding obtained in the present study on the effects of a plane boundary might be valuable to address solidification of polydispersed suspensions. Indeed, in suspensions involving particles of very different sizes, large particles might play the role of an extended smooth boundary for small particles in a way analogous to that played by the sample plates on particles here. Then, noticeable implications on the density of small particles and on the mechanics of the whole suspension may be expected. In particular, one may anticipate that the mean distance between large particles will play the role of the sample depth $e$ here, so that large effects on the layer thickness and on the pressure of the particle matrix may be expected if this distance stands of the order of the influence length $\lambda \approx 9d$ with respect to the small particles of diameter $d$.

VI. CONCLUSION

Freezing monodispersed suspensions in directional experiments in thin samples has evidenced that the thickness of the compacted layer formed ahead of the solidification front increases with the sample depth at other parameters fixed. This effect has been related to the inhomogeneity of particle density brought about by the long range correlation order imposed by the sample plates. This leads the particle density to evolve from that of hexagonal packing at the sample plate to that of random close packing far from it.

A mechanical model of trapping provides a link between the layer thickness, the particle inhomogeneity and the sample depth. It has been used to deduce the particle
profile that yields the best fit to the layer thickness evolution. This reveals a somewhat large influence length of smooth boundary of about 9 particle diameter.

Beyond the deepening of the physical analysis of freezing suspensions, these results may be useful to better model polydispersed suspensions when large particles act as smooth boundaries for small particles. In particular, noticeable implications on the density of small particles and on the mechanics of the suspension may be expected if the mean distance between large particles is less than a boundary influence length.

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[49] N. Francois, R. Saadatfar, C. R., and A. Sheppard, Physical Review Letters 111, 148001 (2013).
[50] J. Bernal, Proc. R. Soc. A 280, 299 (1964).
[51] A. Anikeenko and N. N. Medvedev, Physical Review Letters 98, 235504 (2007).
[52] A. Anikeenko, N. N. Medvedev, and T. Aste, Physical Review E 77, 031101 (2008).