Intellectual properties of a granular nanoporous medium in a non-wetting liquid.

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Abstract. The intellectual properties of a suspension of a granular nanoporous medium in a non-wetting liquid under conditions of a pulsed pressure change are discussed in the work. The characteristic response time (0.1 ÷ 10) ms and the high specific energy intensity of the impact energy conversion (E) (10 ÷ 100) J / g make attractive the use of such type suspensions in shock / explosion absorption devices. In the process of rapid compression upon impact and when the critical pressure (P0) is reached, the suspension is transformed into a new state with a change in the compressibility (χ = dV / dP) by (2 ÷ 4) of the order. In the new state, the process of volume reduction does not depend on the temperature and viscosity of the liquid, it is practically non-dissipative and at constant pressure. A microscopic mechanism of such a nontrivial nonlinear response is proposed. The intellectual properties of a suspended granular nanoporous medium in a non-wetting liquid under conditions of pulsed pressure changes are considered using of the Libersorb 23-water system as an example.

1. Introduction
According to [1] the intellectual materials it is materials satisfying the following conditions: 1. Intellectual material is created by synthesizing various components to obtain the required response; 2. Strong response to external impact; 3. The macroscopic properties of the response and the change in state must be determined by a microscopic mechanism; 4. After the response, the intellectual material must return to its initial state.

At the present time, intelligent materials are known with the use of the effects of change under the external influence of the properties of a flat or rough surface of materials [1]. For example, when the surface is chemically modified by polymer molecules, the self-cleaning effect of the surface is observed. This is achieved due to the mechanism of changing the conformation of grafted polymers to the surface with increasing temperature [2]. As a result, the surface changes from a hydrophilic state to a hydrophobic state at a low temperature as the temperature rises and self-cleaning of the surface is observed.

As it follows from the results of a study of the properties of three materials of granular nanoporous media, different in nature, in a non-wetting liquid [3] in its design, response to impact and microscopic mechanism of state change during impact, and these materials can be attributed to new intellectual materials. It should be noted that the characteristic time for the outflow of non-wetting liquid from a
granular nanoporous materials can be \((10^4 \div 10^7)\) s \([4, 5]\), but also and \((10^2 \div 10^3)\) s at the characteristic filling time \((10^4 \div 10^3)\) s \([3, 6]\).

Another attractive feature of such materials is the high (up to 100 J/g) specific energy consumption of the process of filling nanopores of granules at the excess pressure. It follows that the suspension of a granular nanoporous medium in non-wetting liquid can be used for multiple impact absorption as a material with a response time comparable to the impact time. However, questions about the choice of properties and under what conditions the material under discussion can demonstrate intellectual properties that differ fundamentally from the properties of irreversibly (or viscoplastic) deformable materials \([7]\). First of all, this is a response to a shock pre-programmed with a material that allows providing the force (pressure) of an impact on the protected object that is smaller than the energy (impulse) impact, without reference to its magnitude. This possibility is indicated by the results of \([3, 6, 8]\). However, in experiments \([9, 10]\) under different conditions, a strong pressure-force dependence on the time under impact and on the characteristics of the liquid and the mass of the porous substance was observed for the granular nanoporous substance in the various liquids studied. Therefore, the question of the properties of the response of a granular porous medium suspended in a non-wetting liquid remains open.

2. The developing for providing of necessary response

The basic and necessary property for a nanoporous granular material is lyophobicity. This property can be both natural and obtained by modifying the surface of the nanoporous granular material. Thus, the investigated system Libersorb 23 (L23) - water consists of a porous material L23, which is a silica gel KSK-G with a SiO\textsubscript{2} frame material, the surface of which was chemically modified by alkylsilanes according to the procedure described in \([11]\), to impart a hydrophobic property to the pore surface. Lyophobicity of this material to the water was confirmed in \([12]\). In addition to the necessary condition for the surface to liquid to be lyophobic when creating a material with predetermined properties, it is also necessary to know the specific pore volume of the porous medium \((V_{\text{por}})\), the compressibility of the porous medium \((\chi_{\text{pm}})\) and the liquid \((\chi_{\text{liq}})\), the characteristic of the pores filling pressure \((P_0)\) and the evidence of returning the system to its initial state after an external impact. Characteristics of the L23 - water system are as follows: \(V_{\text{por}} = 0.56 \pm 0.02\) cm\(^3\)/g, \(\chi_{\text{pm}} = 0.41 \times 10^{-8}\) 1/MPa, \(\chi_{\text{liq}} = 4.4 \times 10^{-8}\) 1/MPa \([13]\), \(P_0 = 16 \pm 1\) MPa. It was also shown in Ref. \([12]\) that the system returns to its initial state after pores filling with a non-wetting liquid, and the fraction of non-liquid is less than 5% at a temperature of 20 \(^\circ\)C. Subsequent drying of the L23 samples showed their complete recovery to the initial state. Also in work \([6]\) for this system it was found that when the impact is applied and the mass of the porous medium is sufficient, the pores filling pressure of the non-wetting liquid remains, up to the complete absorption of the impact energy, constant within the measurement error. Thus, the correct choice of a porous material and a liquid is an important step in the creation of a material, namely a suspension of a porous substance in a non-wetting liquid having a strong response to an external action.

3. Strong response to external influences and return to initial state

An investigation of the response to an external impact during the filling of porous systems with non-wetting fluids was performed on an experimental bench and using the procedure described in \([6]\). A typical record of the change in pressure time \((P)\) and a decrease in the volume \((-\Delta V)\) of a suspension of granular nanoporous material L23 (4 g) in a non-wetting liquid, water (55 cm\(^2\)), as a result of a 10 kg load impact with an energy of \(E = 30\) J is shown in Fig. 1a and 1b. It can be seen that as the time increases in the process of impact due to the movement of the rod inside the chamber, volume decreases with a continuous increase in pressure to point 2 in Figs. 1a and 1b. In point 2, the mode of transformation of the impact energy is changed. Continuous growth of pressure with a decrease in volume is replaced by a decrease in volume at a constant, within the error of measurement, independent of time and pressure. Therefore, point 2 is the critical point at which the "compressibility" \((\chi = d\Delta V/dP)\) (receptivity) of the material suspension in the liquid changes abruptly with a continuous
decrease in volume. The volume of suspension of the granular material and liquid continues to decrease at constant pressure with an increase in time to point 3. At this point, the volume decrease volume reaches a maximum. This corresponds to stopping the stock and the load. In the time interval from point 3 to point 4 the stock moves from the chamber so that to point 4 the volume of material and liquid tends to the initial state.

Figure 1. The experimental data of the pressure change in the chamber (a), and the internal volume of the chamber (b) versus time. The chamber is filled with water (liquid volume 55 cm³) and a porous medium L23 with a mass of 4 g. The impact energy $E = 30 \pm 2$ J.

As it follows from Fig. 1b in the time interval from point 0 to point 2, with a pressure increase to the value $P_2 \approx 18$ MPa, the volume decrease was $\Delta V_{0,2} = 1.104 \pm 0.05$ cm³. Estimates show that the volume change in the time interval from point 0 to point 2 due to the elastic deformation is equal to $\Delta V_{el} = 1.05 \pm 0.05$ cm³, and within the measurement error coincides with the measured value. From this it can be concluded that in the time interval from point 0 to point 2 the possible value of the volume of filled pores lies in the range $(2 \div 3)\%$ in accordance with the measurement error.

In the time interval from point 2 to point 3 the pressure does not change. Therefore, the observed volume change cannot be related to elastic deformation and the volume decrease by $\Delta V_{2,3} = 1.14 \pm 0.05$ cm³ is due to the filling of nanopores granules with liquid. Knowing the value of $\Delta V_{2,3}$ makes it possible to estimate the fraction of the impact energy transformed into the energy expended for the pores filling $E_{2,3} = P_{2,3} \cdot \Delta V_{2,3} \approx 20.5$ J. This value, together with the estimates of the energy of elastic deformation on the time interval from point 0 to point 2, equal to $E_{el} \approx 10$ J, give, within the error of measurement, the value of the impact energy $E = 30 \pm 2$ J.

The filling pores energy $E_{2,3}$ spends to creation of the nonwetting liquid - the framework of the porous medium surface in the filled pores, the meniscus liquid-gas surface, and the liquid flow $J = d\Delta V/dt$. As the filling increases, the surface of the frame-liquid interface increases and the kinetic energy of the load decreases. When the filled volume is increased, pores of smaller size should be filled and at a higher pressure in accordance with the Laplace formula. Therefore, one could expect an increase in the filling pressure in the interval from point 2 to point 3 with increasing time, rather than a constant $P = P_{2,3}$. Alternatively, according to [6], transport channels from such multiparticle local pore configurations are filled throughout this time interval, which consist of all pores of different sizes in accordance with the pore size distribution. The constant value of the pressure corresponds to the constant value of the total filling flux $J = d\Delta V/dt$ under the assumption of a constant hydrodynamic resistance over the entire time interval from point 2 to point 3 with the exception of the vicinity of point 3 of stopping filling (stopping the stock), see Fig. 1. Another part of the energy is expended, apparently, on the provision of liquid transport and on heat release as a result of the formation of a liquid-frame surface of a porous medium and liquid-gas [14] and dissipation during a viscous fluid flow. Also, in order to understand the nature of this phenomenon, additional experiments were performed to fill the granules at a various temperatures.
It is known that in the temperature range \((5 \div 60) ^\circ C\) [13] the coefficient of water viscosity varies three times. Therefore, we could expect a change in the pressure-time dependence upon impact with a decrease in temperature from 55 to 7 C. However, the \(P(t)\) dependences for the water of the granular material L23 within the measurement error at \(T = 7^\circ C\) and \(T = 55^\circ C\) were the same (see Fig. 2a), which coincides with the result for the system of an aqueous CaCl$_2$-L23 solution [6]. On this basis, it can be assumed that water transport in nanopores with an average radius of 5 nm does not depend on the viscosity of the liquid in the regime of rapid compression upon impact. Similar results were observed for nanoporous hydrophobic zeolite granules and Silica gel in water and glycerol in [9, 15]. Since the flow of liquid when filling the pores with rapid compression is independent of temperature and therefore of viscosity, the main source of thermal effects can be heat release and heat absorption when forming the liquid-frame boundary of the porous medium and liquid-gas during filling [14]. It was shown in [16] that the energy of heat release when the number of nanoporous media is slowly filled makes up several percent of the filling energy.

Figure 2b shows the results of the pressure change from the time of the investigated system at \(T = 55^\circ C\) without replacing the porous medium and the fluid for impact No.1 and impact No. 5. As the results coincide within the measurement error, we can conclude that the system returns to its original state after the response to external influence.

From the dependences presented on Fig. 2 and additional experiments it follows that the critical filling pressure \(P_0\) for the system under investigation does not depend on the temperature, fluid viscosity and the number of impacts with a constant impact energy. The transformation of impact energy by a granular nanoporous material in a non-wetting liquid occurs at constant pressure by an essentially non-dissipative filling process that begins at the critical pressure \((P_0\) in Fig. 1). These pressures determine the pores filling threshold, at the percolation cluster formation pressure, described in percolation theory [17].

In the quasistatic regime, in accordance with [18], pores filling with a non-wetting liquid occurs at \(P \approx P_{c0}\) at the percolation threshold and under the condition that the characteristic time \((\tau_0)\) of the pressure increase is close to the characteristic filling time \((\tau_V)\). Under these conditions, the increase in pressure does not depend on the speed of the faster process of elastic compression and is determined by the slower process of volume reduction due to filling. Another situation with rapid compression is when, in the time interval \(t_0\) - \(t_2\), the pressure increase may outstrip the filling. Therefore, we can assume that the liquid-granular material system skips the quasistatic filling point and is "thrown" into the new state at a new critical pressure \(P_0 > P_{c0}\) when the bound nanopores of the granules are filled without changing \(P\), i.e., at constant pressure. This filling is analogous to the spontaneous filling of the pores of the medium with a wetting liquid.
The additional experiments carried out on the L23-water system at different impact energies and the mass of the porous material showed that the pressure $P_0$ within the measurement error does not depend on the impact energy $E$ or on the mass L23. As a result, the independence of $P_0$ from the impact energy and the sample mass implies that the critical pressure $P_0$ is constant and the filling rate in the vicinity of $P_0$ is not limited by the transport of liquid through the surface of the granules. Therefore, the critical point at $P_0$ is the point of transition to spontaneous filling when the filling rate is determined by the hydrodynamic resistance of the nanopores system. At a time $t > t_3$ and at $P = P_0$ the rate of such filling becomes higher than the elastic compression rate and does not depend on the viscosity of the liquid.

In Fig. 3 shows the time dependence of the pressure $P(t)$ and the volume change $-\Delta V(t)$ for the system, the granular material L23 (4 g) in water (55 cm$^3$) at $T = 20^\circ$C for the impact energy $E$ from 5 to 70 J. It is shown, that the $-\Delta V(t)$ dependences differ by different time $t_3$ of reaching the maximum of the values ($-\Delta V_{\text{max}}$), the degree of symmetry at the maximum, and different derivatives of the volume dependence on time. When the energy of impact $E$ increases, the transition from the $P = \text{const}$ dependence to the $P(t)$ dependence is close to linear over the time interval from point 1 to point 2. For the energy $E = 5$ J, the dependences $P(t)$ and $-\Delta V(t)$ are symmetric at the maximum $t_3 = 18$ ms. The magnitude of the maximum pressure $P(t_3) = 12.5$ MPa is less than the pressure of the start of pores filling in the L23-water system equal to $P_0 = 18$ MPa and the pressure of the pores filling start in the quasistatic mode $P_{c0} = 15$ MPa. Therefore, at $E = 5$ J, the filling conditions do not arise. Close to the symmetric dependence $-\Delta V(t)$ is also characteristic for the transformation of the impact energy into the elastic energy of the system.

**Figure 3.** Dependences a) $P(t)$ and b) $-\Delta V(t)$ for the system L23 (4 g) - water (55 cm$^3$) with impact energies of 5, 20, 50, 60 and 70 J at a temperature of 20 °C.

At an energy $E$ from 20 to 50 J, pores are filled at constant pressure. The filling at $P = \text{const}$ at the time $t_3$ reaches the maximum $-\Delta V(t)$. This is the moment of stopping the movement of the stock in the chamber and its subsequent return motion. Also a third qualitatively different regime for the transformation of the impact energy can be observed. At an energy $E = 70$ J, the compressibility of the system changes abruptly in point 1 at $P = 18 \pm 1$ MPa. This value coincides with the value of the critical pressure $P_0$ at lower energies. As the time increases after point 1, the pressure does not remain constant, but increases according to a law close to linear to a value $P = 22$ MPa in point 2. This increase in pressure is accompanied by a change (decrease) in the volume $\Delta V_{1-2} = 2.2 \pm 0.1$ cm$^3$, the value of which, within the error of measurement, is close to the value of the total pore volume of the sample ($\sim 2$ cm$^3$), taking into account the volume change due to elastic compression ($\sim 0.2$ cm$^3$). After point 2, the pressure and volume changes increase, reaching simultaneously a maximum in point 3 and then decrease to the original values. The magnitude of the volume change and the symmetric form of the $P(t)$ and $-\Delta V(t)$ dependences near the maximum in the time interval from point 2 to point 3 correspond to elastic compression. The total energy of transformation at the section 0 - 1, 1 - 2, 2 - 3 to the point of load stopping within the measurement error coincides with the kinetic energy of the load.
In the energy conversion mode, when filling nanopores at constant pressure and increasing the impact energy at \( E < 50 \text{ J} \), the pores filling rate, \( J = \frac{d\Delta V}{dt} \), increases. This is due to the fact that with increasing impact energy, the speed of stock movement into the chamber increases and, consequently, the rate of decreasing of the volume of the system. Therefore, at a constant pressure and, consequently, a zero volume change due to compression, the pores filling rate of the pores of the granules is determined experimentally as the rate of decrease in the volume of the system. In accordance with Fig. 3b, the value of \( J(t) \) as a function of time is close to linear in the entire time interval 0 - 1 except for the vicinity of the maximum \(-\Delta V\). Since the pressure difference that initiates the filling of empty pores can be assumed equal to the measured pressure, the relation \( P = J \cdot \rho \) should be satisfied, where \( \rho \) is the hydrodynamic resistance to filling the pores system in all granules. Then for \( \rho = \text{const} \), the increase in the flux \( J \) should lead not to the observed constancy of the pressure, but to its increase. Either the increase in \( J \) should cause a nonlinear response in the form of a decrease in the pores filling resistance \( \rho \), and then \( P = \text{const} \), taking into account the independence of the flow from the viscosity of the liquid. This response was proposed in [5] and will be discussed in Section 4.

Thus, it follows from the foregoing that there exists a maximum flux \( J \) in the spontaneous-filling mode at \( P = \text{const} \). We note that when the impact energy \( E \) increases, the value of \( J \) tends toward the maximum value determined by the maximum of the slope angle \(-\Delta V(t)\).

4. Microscopic mechanism

The dynamics of filling with a non-wetting liquid nanopores granules is described in [6] with the aid of a system of kinetic equations for the distribution functions of clusters in terms of the number of available pores in them and clusters of filled pores. By available pores, by definition, are pores that are formed without delay (instantaneously) in accordance with the magnitude of the pressure. In contrast to them, the filled pores are formed after a finite time, necessary for pouring in and filling the pores with liquid.

As the hydrodynamic pressure in the nanopores system increases, the number and size of clusters from the available pores increase, and the process of their growth is described as the fusion ("interaction") of such clusters. This is a process with a characteristic time that coincides with the time of pressure increase. The process of the disappearance of clusters of accessible pores and the formation of clusters of filled pores is described as the process of filling the liquid with available pores through neighboring clusters of filled pores. The characteristic time of these processes is the hydrodynamic time of fluid motion and the filling of a cluster of accessible pores.

There are three processes with different characteristic time scales. This characteristic time \( \tau_P \) is inverse to the value of the pressure growth rate, the characteristic time \( \tau_k \) is the growth in the number of clusters from a finite number of filled nanopores and the characteristic time \( \tau_V \) of the change in the macroscopic volume. In view of the relative smallness of the volume of clusters from a finite number of filled pores, \( \tau_k << \tau_V \). The ratio of the times \( \tau_P \) and \( \tau_V \) can be controlled in experiments, since these quantities are related by the relation:

\[
\tau_P = \frac{P}{dP/dt} = \frac{V}{dV/dt} \cdot \frac{P}{V \cdot dV/dP} = \tau_V \cdot \chi.
\]

Here, \( \chi \) is the compressibility of the suspension with a volume \( V \) at a pressure \( P \). The reason for the compressibility of the suspension can be either an elastic compression of the liquid and granules, or a change in the volume of liquid in the pores.

In experiments with the studied systems (see Fig. 3), when the impact is absorbed in the time interval 0 - 1, a linear dependence of pressure on time and changes in the volume of suspended matter is observed. This dependence corresponds to the elastic compression of liquid and granules with unfilled pores. For the systems studied in the experiments, \( \chi = \left(10^{-4} \div 10^{-2}\right) \). Therefore, the characteristic growth time of the pressure \( \tau_k \) is the filling time, and the rate of pressure growth is higher than the filling rate. As a result, the liquid-nanopores systems of the granules "slip" through the percolation threshold (Fig. 1a) in the quasistatic filling mode at a pressure of \( P_{\text{c},0} < P \).

In the vicinity of point 2 (Fig. 1a) when the pressure value \( P_0 \geq \text{P}_c \) should be observed dynamic percolation transition [6] (\( \text{P}_c \) - dynamic pressure percolation threshold). In the vicinity of the dynamic
percolation \( P_0 \) transition at \( \geq P_c \) clusters arise from filled pores. When passing through the point of dynamic percolation threshold in the neighborhood of this point sharply changes (Fig. 1a) the slope of \( P(t) \) at constant \( dV/dt \), and changes by many orders effective compressibility \( \chi \) suspensions. Therefore investigated in the time interval (Fig. 1, 2 - 3) the values of the characteristic times of change in pressure and volume of the same order: \( \tau_P \sim \tau_V \) and the rate of change of pressure follows the rate of change in volume when nanopores are filled. This time relationship also means that the filling rate exceeds the deformation rate, and if the pressure \( P_2 = P_3 = \text{const} \) is unchanged, deformation does not take place. Thus, when passing through the point of the dynamic percolation transition, the suspension is in a state where the transformation of the energy and momentum of the impact due to the filling of nanopores can be effective at high impact rates than with deformation.

In accordance with [6], the state of suspension of nanoporous granules beyond the threshold of dynamic percolation can be called a state of spontaneous filling. In this state, the filling rate exponentially depends on time with an exponent proportional to the number of clusters of filled pores. Such a mode in the dynamics of a percolating system is formed because the more the number of clusters of filled pores and the faster they are formed, the faster the "infinite" percolation cluster of available but empty pores is filled. Qualitatively, it can be said that as the rate of decrease of the volume \( J = d-\Delta V(t)/dt \) increases and, consequently, the filling rate with increasing impact energy/momentum, the "number of filling channels" starting from clusters of filled pores increases. Therefore, we can also say that an increase in \( J = d-\Delta V(t)/dt \) should lead to a decrease in the hydrodynamic resistance to motion of the non-wetting liquid in the disordered system of nanochannels of the granules. This apparent constancy of the resistance is obviously related not to a change in the viscosity of the liquid, but to an increase in the number of "filling channels". As a consequence, as the pores filling rate \( J = d-\Delta V(t)/dt \) increases, the hydrodynamic (not viscous) resistance decreases, and the driving fluid the hydrodynamic pressure drop \( \delta P = P_2 - \text{O}_2 \text{-hydrodynamic pressure in empty pores, remains constant. This is precisely what is observed in the experiments carried out, if the maximum possible for suspension flow rate for spontaneous pores filling is not attained at impact. The maximum filling rate is determined by the maximum number of channels beginning at the surface of the granules and depends on the porosity of the granules.}

5. Conclusion
Proceeding from the foregoing, it can be concluded that the suspension of a granular nanoporous medium in a non-wetting liquid under conditions of a pulsed pressure change exhibits intellectual properties and can be considered an intellectual material.

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References
[1] Wang P (Ed.). (2016). Smart materials for advanced environmental applications. Royal Society of Chemistry.
[2] Ou R., Wang Y, Wang H and Xu T 2013 Desalination 318 48-55
[3] Borman V D, Belogorlov A A, Tronin V N 2018 Colloids and Surfaces A: Physicochemical and Engineering Aspects 537 540-548
[4] Borman V D, Belogorlov A A, Tronin V N 2016 Colloids and Surfaces A: Physicochemical and Engineering Aspects 496 63-68
[5] Borman V D, Belogorlov A A, Tronin V N 2016 Physical Review E 93(2) 022142
[6] Borman V D, Belogorlov A A, Lisichkin G V, Tronin V N, Troyan V I 2009 Journal of Experimental and Theoretical Physics 108(3) 389-410
[7] Evans A G, He M, Deshpande V S, Hutchinson J W, Jacobsen A J, Carter W B 2010 *International Journal of Impact Engineering* **37** 947-959
[8] Borman V D, Belogorlov A A, Grekhov A M, Tronin V N, Troyan V I 2001 *Journal of Experimental and Theoretical Physics Letters* **74** 258-261
[9] Xu B, Qiao Y, Chen X 2014 *Journal of the Mechanics and Physics of Solids* **62** 194-208
[10] Surani F B, Kong X, Panchal D B, Qiao Y 2005 *Applied Physics Letters* **87** 163111
[11] Lisichkin G V, Fadeev A, Nesterenko P N, Serdan A A, Mingalev P G, Furman D B 2003 Khimiya privykh poverkhnostnykh soedinenii (Chemistry of surface grafted compounds, in Russian).
[12] Borman V D, Belogorlov A A, Byrkin V A, Tronin V N, Troyan V I 2012 *JETP letters* **95** 511-514
[13] Haynes W M (Ed.) 2014 CRC handbook of chemistry and physics. CRC press.
[14] Borman V D, Belogorlov A A, Byrkin V A, Lisichkin G V, Tronin V N, Troyan V I 2011 *Journal of Experimental and Theoretical Physics* **112**(3) 385-400
[15] Han A, Lu W, Punyamurtula V K, Chen X, Surani F B, Kim T, Qiao Y 2008 *Journal of Applied Physics* **104**(12) 124908
[16] Gomez F, Denoyel R, Rouquerol J 2000 *Langmuir* **16** 4374-4379
[17] Sahimi M. 1993 *Reviews of modern physics* **65** 1393
[18] Borman V D, Belogorlov A A, Grekhov A M, Lisichkin G V, Tronin V N, Troyan V I 2005 *Journal of Experimental and Theoretical Physics* **100** 385-397