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TOWARD THE ANALYSIS OF THE STRUCTURE OF GRANULAR MATERIALS

The structural ordering, which is observed in granular materials and some other soft-matter objects (e.g., dusty plasma) on the meso- and macroscales, has been studied using geometrical methods (Voronoi diagrams) and by analyzing the structural order parameters. The phase diagrams for the translational and orientational order parameters testify to the native anisotropic character of granular materials. The model of lattice gas entropy has been used to describe the vertical density distribution in granular materials in a gravitational field. The obtained theoretical results agree well with experimental data and reproduce them in the nearest vicinity of the states with maximum packing.

K e y w o r d s: granular systems, local structure, structural transformations, order parameter, phase diagrams, anistropic phase, configurational entropy

1. Introduction

Granular materials (GMs) are conglomerations of a large number of discrete particles, granules, with the spread of their sizes extending from a few micrometers to several meters. Granules interact with one another mainly owing to particle-to-particle contacts. In most cases, those contact interactions are nonlinear. A characteristic feature of GMs consists in that the contact interactions between granules are, generally speaking, dissipative. Therefore, such systems are non-equilibrium even at rest, actually being in metastable states. The role of main energy scale in GMs is played by their energy in an external (gravitational) field, which together with boundary conditions ultimately govern the GM shape. If the energy supply from the environment is ceased, the kinetic energy of granules vanishes almost instantly. Hence, GMs are not true thermodynamic systems.

Under specially created conditions, GMs are dissipative discrete micromechanical dynamic systems. They demonstrate properties that are both typical of aggregates of condensed matter states (such as gases, liquids, and solids) and basically different from them. Such a multicomponent behavior of GMs makes the task of describing their properties in the framework of a consistent theory very difficult. Despite a few successful models, the problem remains far from its ultimate solution [1–4].

As a consequence, the industrial technologies of GM treatment – more precisely, their theoretical substantiations – are mainly based till now on the summarizing of empirical data concerning their behavior under various external conditions. For instance, let us consider such a well-known and illustrative property of GMs as their compaction, which consists in a reduction of the volume occupied by the system after its treatment in an external field of mechanical perturbations. It is evident that the understanding of the physical nature of only this property would already allow the efficiency of GM applications in industry to be improved substantially and a considerable progress in the theory development to be made. It should be noticed that the researches of some other soft matter objects (GMs represent one of their kinds) – e.g., dusty plasma, which essentially differs from the GMs described above by the character of the particle-to-particle interaction – allowed the existence of structural order-

ing isomorphic to that observed in GMs to be established.

The local structure of a condensed substance substantially governs its behavior at the macro-scale level. In particular, it affects the structure formation, phase transformations, and dynamics in the material. As a rule, the kinetics of structural transformations effectively develops on the so-called mesoscale, where the processes of formation or destruction of defects, domains of another phase, and so on start. Therefore, the structure parametrization on the mesoscale (in the sense defined above) is an essential element on the way to simulate the structure and the dynamics of condensed matter objects. In the case of GMs, we have a unique opportunity to observe structural modifications that takes place under the influence of external perturbations and do it with an almost naked eye. The simulation of the structure and the transitions between various structure types demands that a multiscale analysis be applied.

In experiments with magnetic fluids that are subjected to the action of an external magnetic field and a vibrational shaking field [6], a structurization with a symmetry of the hexagonal type was observed in droplets. In work [7], the analogous ordered structures, which consisted of water droplets levitating over the heated-up surface of water at a temperature close to the boiling one, were registered. Similar features revealed in the structure formation at the mesoscale level in the systems, which are so different by their physical nature, can be induced by the action of isomorphic mechanisms (e.g., the excluded volume effect) under definite conditions. Below, we shall analyze some analytical methods of structure parametrization and the results of their application to two-dimensional (2D) GMs and dusty plasma.

2. Structure of 2D Granular Materials and Dusty Plasma

The researches of 2D meso- and macroscaled soft-matter objects – granules, dust particles, hard disks, water and magnetic fluid droplets – allowed the presence of such states in their structure to be established, which are, from the viewpoint of the character of particle distributions in them, either typical of or different from regular aggregate states (gases, liquids, and solids). Transitions between the states with different, by symmetry, characters of local ordering occur following various scenarios depending on the initial state (more exactly, on the initial compaction in the case of GMs), the dimensionality, and the intensity of dissipative losses (or their absence).

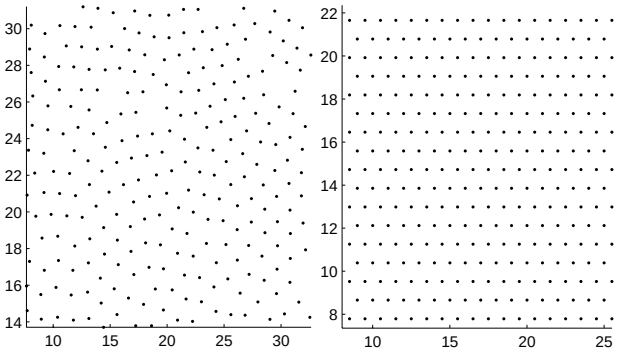

Fig. 1. Structures observed in a two-dimensional system of hard disks perturbed externally by shaking it in the horizontal direction (digitized, arbitrary selected stroboscopic photos of the system): the initial disordered state (left panel) and a state with the hexagonal symmetry (right panel)

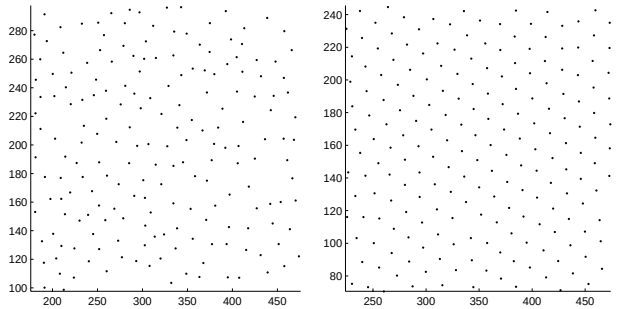

Fig. 2. Structures observed in 2D dusty plasma (according to the results of work [5]): the initial disordered state (left panel) and a structure with dominating domains of the hexagonal symmetry (right panel)

In the course of experimental researches, a micromechanical system consisting of hard disks located in a horizontal plane was perturbed by shaking it in this plane. The disk diameter was 17 mm, and a rectangular cuvette containing the disks had linear dimensions of 16.5×20 cm^2. The initial disk distribution over the cuvette had a stochastic character. After the energy supply from the outside was ceased, the system stopped, and the disks were photographed. In Fig. 1, the data obtained as was described above are exhibited. The figure evidently demonstrates the formation of clusters with a hexagonal symmetry in the arrangement of granules.

It is interesting to note that the formation of a similar structure was observed in systems that are basically different from GMs, in particular, in

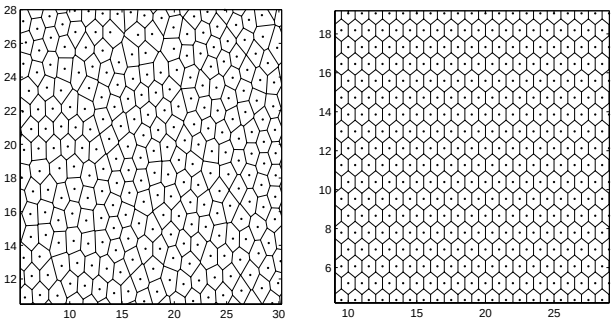

Fig. 3. Voronoi cells for structures observed in a 2D system of hard disks perturbed externally by shaking it in the horizontal direction: the initial disordered state (left panel) and diagrams corresponding to a structure with the hexagonal symmetry (right panel)

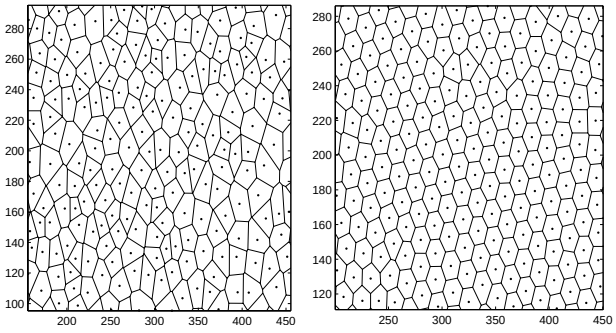

Fig. 4. Voronoi cells for structures observed in 2D dusty plasma (according to the results of work [5]): the initial disordered state (left panel) and a structure with dominating domains of the hexagonal symmetry (right panel)

dusty plasma. In Fig. 2, the analogous structures, which were experimentally observed while studying the structure formation in a system consisting of particles in dusty plasma, are depicted.

The formation of local structures belonging to various types, as well as their evolution on the meso- and macroscales, is convenient to be analyzed using the Voronoi method. The construction of Voronoi cells consists in determining such a space around the particle center, which includes all the points that are the closest to this center [8]. Figures 3 and 4 exhibit Voronoi cells that correspond to the distinguished types of structures in 2D GMs and dusty plasma, which were shown in Figs. 1 and 2.

The analysis of data presented in Figs. 1 to 4 testifies that the structure formation in those systems, which are different by their physical nature, has certain similar features at the mesoscale level. For instance, the formation of a short-range order in the

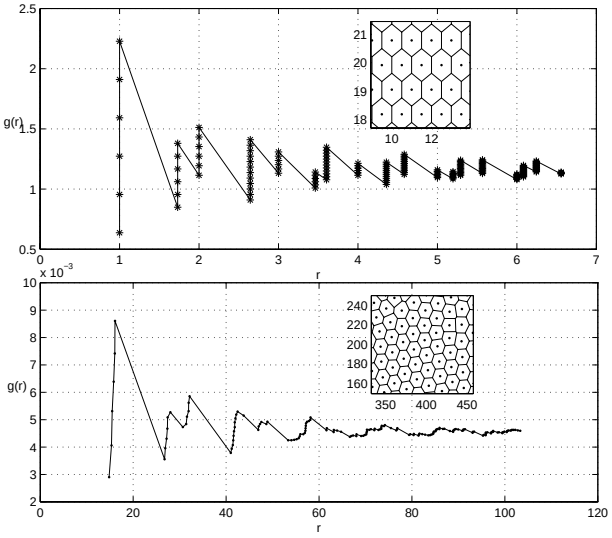

Fig. 5. Function $g(r)$ for granular materials (upper panel) and dusty plasma (lower panel). The insets illustrate the Voronoi cells for the corresponding structures

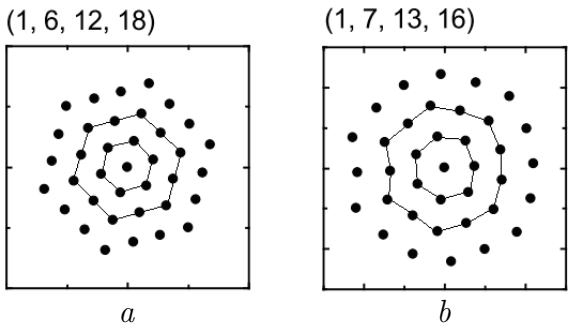

Fig. 6. Types of local structure observed in 2D systems of hard disks

local structure is observed in both cases, with the creation of more symmetric structures corresponding to a higher symmetry of Voronoi cells. In the cases of crystallization of particles (impurities) in dusty plasma and particles (granules) in a granular system, the Voronoi diagrams mainly demonstrate the hexagonal symmetry on the mesoscale with quantitatively different perimetric parameters.

The structurization can be described illustratively by calculating the function $g(r)$ [9]. For the considered systems, the results of calculation of this function are shown in Fig. 5. The analysis of the data exhibited in this figure testifies that the density distributions in the examined systems correspond to the formation of shell structures in both of them.

For instance, let us consider a 2D packing of hard disks on a plane (points in Fig. 6 denote the posi-

tions of disk centers). Let us select a particle and postulate that it completely fills the first conditional shell. The group of the nearest neighbor particles around it creates the second structural shell. Figure 6 demonstrates states which are observed in a system of two-dimensional disks on the mesoscale. If the ordered structure around the central particle looks like that shown in Fig. 6,*a*, there are six neighbor particles in the nearest vicinity of the central one, which can be interpreted as the second shell. In the next, third shell, there are 12 particles. In the framework of this shell approach, the structure in Fig. 6,*a* can be classed as (1; 6; 12), where the numbers indicate the filling degrees for the corresponding shells. Note that the considered structure was crystal-ordered. Accordingly, the structure shown in Fig. 6,*b* should be classed, as (1; 7; 13). In such a manner, structural changes of the ordering-disordering type, as well as transitions between ordered states with different symmetries in a particle arrangement, can also be described in the framework of the shell model and in terms of occupation number fluctuations, which are inherent to it. In this approach, the completely filled shells are associated with the most symmetrized states. In the framework of the shell model, the corresponding phase diagram can be plotted in terms of the order parameter ϕ. The latter can be calculated, e.g., using the shell occupation numbers as $\phi = \frac{n_{id}-n_i}{n_{id}+n_i}$, where n_{id} is the number of particles in the shell when the system is in the symmetrized state, and n_i the actual number of particles in the shell.

Quantitative changes in the area distribution of Voronoi cells, which take place owing to the structural modifications on the mesoscale, can also be described also with the help of the trial function $N(s)$, which looks like

$$N(s) = \frac{b^a}{\Gamma(a)} s^{a-1} \exp(-bs), \qquad (1)$$

where $s = S_V/S_h$ is the normalized area of a Voronoi cell, S_V the area of a Voronoi cell for a specific particle in the observed state, and S_h the area of a Voronoi cell in the case of a system with the hexagonal ordering.

The parametrization of the observation data with the use of function (1) is reduced to the determination of corresponding values for the parameters a and b. The behavior of the distribution function (1) for systems with different packed fractions is shown in Fig. 7. From the result depicted in this figure, it follows that the growth of the packed fraction η is accompanied by a reduction in the dispersion of the corresponding distribution (1). Figure 8 demonstrates the distribution dispersion D as a function of the packed fraction η.

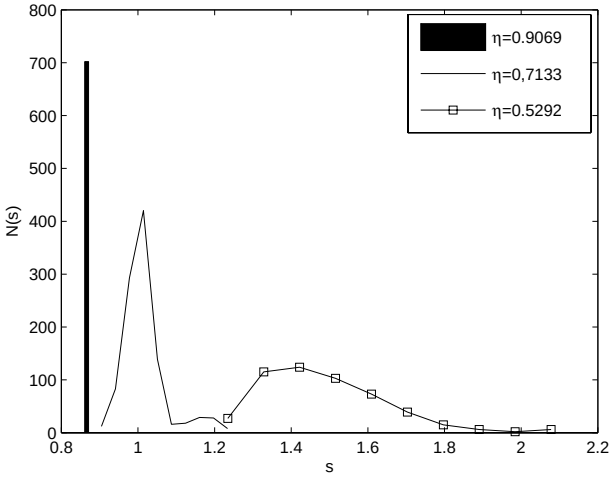

Fig. 7. Characteristic distribution function $N(s)$ for 2D granular materials with various packed fractions

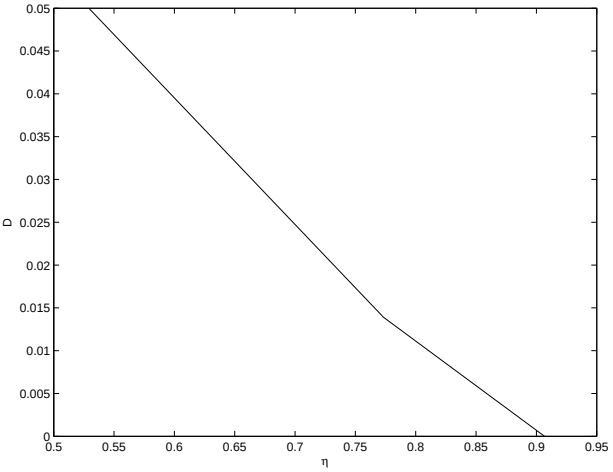

Fig. 8. Dependence of the $N(s)$-distribution dispersion on the packed fraction

It is typical that the features of the characteristic function described above are common for the vicinities of those states, from which a transition to the ordered state takes place, irrespective of the essential difference between the physical nature of the systems under consideration.

3. Model of Lattice Gas Entropy for the Description of Granular Material Densities

A perturbation of the granular system gives rise to its compaction, i.e. to a reduction of the volume oc-

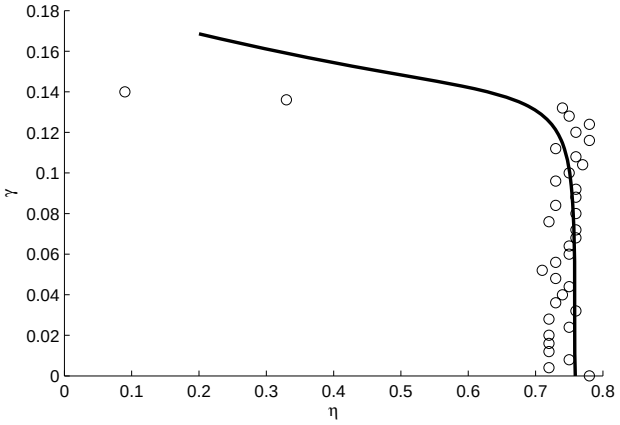

Fig. 9. Dependence of the parameter γ calculated by formula (7) on the packing parameter. Symbols exhibit the experimental data [13]

cupied by the system [10]. From this viewpoint, the issue arises concerning the theoretical substantiation and the parametrization of this phenomenon. We use the quasistatistical approach to the description of the GM density. On this way, let us write down the expression for the free energy functional for a system in the so-called "inherent" states [11] in the form

$$F(\rho) = E(\rho) - \beta^{-1} S(\rho), \tag{2}$$

where the energy of the system in a gravitational field is given by the expression

$$E(\rho) = mg \int\limits_{(V)} z\rho(\mathbf{r}) d\mathbf{r}, \tag{3}$$

z is the vertical coordinate, $\beta = \frac{1}{k_B T}$ is the energy scale, and ρ is the system density. For $S(\rho)$, we use the known relation for the lattice gas entropy [12],

$$S(\rho) = -\int\limits_{(V)} d\mathbf{r} \left\{ \frac{\rho}{\rho_0} \ln \frac{\rho}{\rho_0} + \left(1 - \frac{\rho}{\rho_0}\right) \ln \left(1 - \frac{\rho}{\rho_0}\right) \right\}, \tag{4}$$

where ρ_0 is the maximum density of the system.

The calculation of the variational derivative $\frac{\delta F(\rho)}{\delta \rho}$ allows the equilibrium density profile to be obtained in the form of a distribution similar to the Fermi function,

$$\rho(\mathbf{r}) = \frac{\rho_0}{1 + ce^{\Gamma z}}, \quad \Gamma = mg\rho_0\beta, \tag{5}$$

where c is a constant, which can be determined by comparing the theoretical results with experimental data. It is the formula of type (4) that was used in work [13] for the parametrization of the results of experimental measurements of the vertical density profile in GMs.

Let us consider our system in a vicinity of the ordered (symmetrized) state. Then the deviation from this state (see Fig. 6,*a*) can be interpreted as a destruction ("melting") of the symmetrized ("crystalline") state (see Fig. 6,*b*). Note that, for the quantitative determination of crystal order destruction in solids (melting), the so-called Lindemann parameter is used as a rule [14]. It is calculated as a root-mean-square deviation of a separate particle from its equilibrium position,

$$\gamma = \sqrt{\left\langle \left(r - \langle r_i \rangle\right)^2 \right\rangle} / L, \tag{6}$$

where r_i is the distance between neighbor particles in the observed state, r the distance between neighbor particles in the symmetrized state, and L the lattice constant. In terms of the model under investigation, the expression for the parameter γ reads

$$\gamma = \frac{\rho_0 c}{\Gamma^2} A(\rho),$$

$$A(\rho) = \rho \frac{\ln^2 \frac{1}{c}\left(\frac{\rho_0}{\rho} - 1\right)}{c\rho_0} - \frac{1}{c} \ln^2 \frac{1}{c}\left(\frac{\rho_0}{\rho} - 1\right) -$$

$$-2\left[\ln c \ln \frac{\rho_0}{\rho} + Li_2\left(\frac{\rho_0}{\rho}\right)\right] -$$

$$-\rho_0 c \left[\rho \frac{\ln c}{\rho_0} - \ln \frac{\rho_0}{\rho} + \frac{\frac{\rho_0}{\rho} - 1}{\frac{\rho_0}{\rho}} \ln\left(\frac{\rho_0}{\rho} - 1\right)\right]^2, \tag{7}$$

where $Li_2(x)$ is the dilogarithmic function [15].

Figure 9 illustrates the dependence of γ on the packing parameter η calculated by formula (7). As follows from the exhibited data, the experimentally obtained dependence of the parameter γ on the density, first, qualitatively corresponds to the predictions of the proposed analytical model and, second, demonstrates that the compaction profile of GM in the gravitational field does not obey the Boltzmann distribution. The variation of the limiting density ρ_0 within the physically reasonable range (in particular, up to the really accessible values of packing parameter) results in a better agreement between the experimental data and the data obtained in the framework of the theoretical model. The really accessible magnitudes of packing parameter in a vertical system of

hard spheres reach a value of 0.78. When approaching the initial conditions to this limit, we make narrower the packing interval, in which the scenarios of structure formation develop. Actually, this circumstance restricts the kinetic degrees of freedom for the motion of particles (granules) and enhances the role of relative configurations and entropic effects corresponding to them. A comparative analysis between theoretical and experimental data testifies that they almost completely coincide in the closest vicinity of the maximum packing in the system (see Fig. 9).

4. Translational and Orientational Order Parameters. GM Anisotropy

Of separate interest in studying the structure of GMs is their organization on the global, i.e. macro-, scale. For instance, in work [16], the structural analysis was carried out with the help of a discrete set of points $\{G_i\} \equiv \{\mathbf{r}_\alpha\}$ (here, $\alpha = 0, 1, 2, ...$) representing the coordinates $\mathbf{r}_\alpha$ of centers of particles (granules) that surround the central particle. The latter, in turn, is located at the origin of the selected coordinate system. In this approach, the geometrical structure $\{G_\alpha\}$ can be determined by comparing it with an alternative set of points $\{\Gamma_\alpha\}$. The set $\{\Gamma_\alpha\}$ should be determined in advance and represents an example of perfectly ordered structures (face-centered cubic, hexagonal close-packed, and so on). Information concerning $\{\Gamma_\alpha\}$ can be obtained in the literature sources dealing with the local structure of selected objects. Note that, for instance, in the case of typical liquids, the choice of $\{\Gamma_\alpha\}$ is very restricted, because information on their local structure is not complete. As to GMs, their structure can be observed rather easily even with a naked eye.

In the framework of the proposed approach, any part of the system can be quantitatively described as a deviation from the selected "perfectly" ordered determined set $\{\Gamma_\alpha\}$. In other words, we may consider any local structure as an excited state of the previously selected "perfectly" ordered object. Variations in the local structure can be formally described by introducing the corresponding local order parameter and plotting the phase diagrams for it.

Returning back to the vector set $\{\mathbf{r}_\alpha\}$, which determines the configuration of particles in the group, let us confine its size by the quantity r_0. The role of r_0 can be played, e.g., by the radii of coordination spheres. Formally, the set $\{\mathbf{r}_\alpha\}$ is already a parameter that describes the structural ordering. It strongly

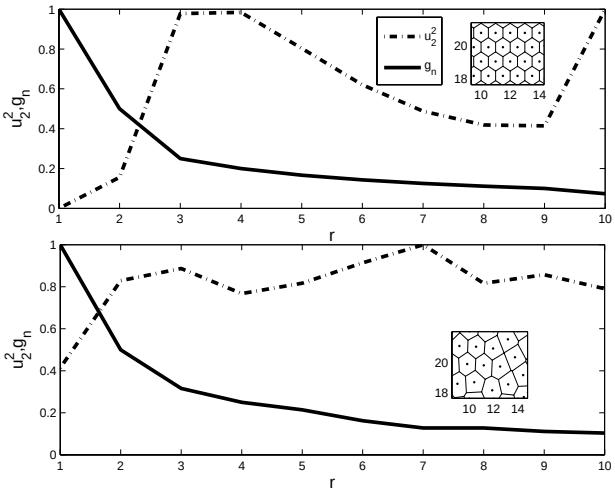

Fig. 10. Order parameters (8) and (9) for granular materials obtained by numerically processing the data depicted in Fig. 1

fluctuates for gases. For crystals, on the contrary, it does not almost change. As a rule, the fluctuations of $\{\mathbf{r}_\alpha\}$, which arise owing to external perturbations in the case of GMs, are supposed to be small enough (of course, here, the matter concerns the orders of smallness different in comparison, e.g., with molecular ones). Moreover, the fluctuations are a consequence of variations in both the lengths of vectors belonging to the set $\{\mathbf{r}_\alpha\}$ and the angles between them.

The orientational and translational order parameters differ from each other. In particular, the orientational order parameter can be defined as follows:

$$g_n = \frac{1}{N_n} \sum_{1}^{N_n} \exp\left(iN_n\varphi_n\right). \tag{8}$$

Here, N_n is the number of particles in the n-th shell, and φ_n is the angle between the radius-vector of a particle in the selected shell and the radius-vector describing the position of the central particle, around which this shell is constructed. On the other hand, the translational order parameter can be written down in the form

$$u_2^2 = \frac{1}{N} \sum_i \left[\left\langle |\mathbf{r}_i|^2 \right\rangle - \langle |\mathbf{r}_i| \rangle^2\right], \tag{9}$$

where N is the number of particles in the shell, $\left\langle |\mathbf{r}_i|^2 \right\rangle$ is the average value of squared distance between the central particle and the i-th particle in the shell, and $\langle |\mathbf{r}_i| \rangle^2$ is the square of the average distance between the central particle and the i-th particle in the shell, for which the measurement is carried out. The classi-

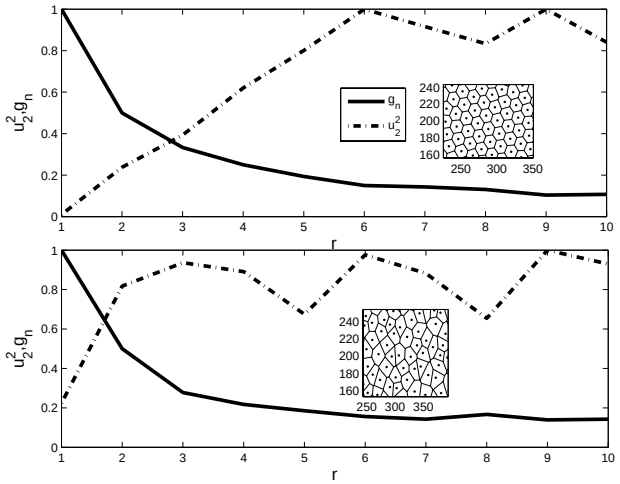

Fig. 11. Order parameters (8) and (9) for dusty plasma obtained by numerically processing the data depicted in Fig. 2

fication of types of local ordering in terms of parameters (8) and (9) was carried out in work [16].

In Figs. 10 and 11, the results of calculations by formulas (8) and (9) for the order parameters in GMs and dusty plasma, respectively, are depicted.

Summarizing the results obtained, we arrive at a conclusion that both examined systems are in anisotropic states with the orientational order parameters different from zero. It is the anisotropic character of those systems and their states that complicates their description in the framework of a consistent theoretical approach. Note that the search for an anisotropic phase in liquids required rather labor-consuming investigations [17]. In the cases of granular systems and crystallized dusty plasma, we deal with the systems that are already in the anisotropic state under natural conditions. The latter circumstance allows the prospects of their application to the problems concerning the transfer of mechanical excitations, waves, and energy to be forecasted.

5. Conclusions

Our study of local structures in GMs and dusty plasma at the mesoscale level using the analytical methods allowing the structure parametrization have shown that the processes of structure formation in soft-matter objects different by their nature reveal certain common features. Namely, the emergence of both short- and long-range orderings is observed in all cases. Since the formation of symmetric structures in packings is accompanied by a symmetrization of corresponding Voronoi cells, the study of structural variations can be carried out with the use of model characteristic functions.

To describe the behavior of the vertical density profile in GMs in a gravitational field, an illustrative combined model of lattice gas entropy is proposed. The phase diagram is plotted in terms of a parameter of the Lindemann type used in the theory of crystal melting and system compaction. The data obtained testify to the adequacy of applying the basic principles of the entropy model to studying the nature of structural transformations in GMs, especially in the case of densely packed systems. Note also that the applied entropy model reproduces the non-Boltzmann character for the density profile of GMs in a gravitational field in a trivial way. The presence of a criterion, which is expressed in terms of the compaction parameter, for the transition into a crystal-ordered state, from which transitions into other states different by symmetry take place, is shown.

By analyzing the behavior of the translational and orientational order parameters, it is shown that the granular materials, dusty plasma, and some other soft-matter objects are the examples of systems which are naturally in anisotropic states.

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ЩОДО АНАЛІЗУ СТРУКТУРИ ГРАНУЛЬОВАНИХ МАТЕРІАЛІВ

Р е з ю м е

Структурне впорядкування, яке спостерігається у мезо- та макромасштабі у гранульованих матеріалах, та деяких інших об'єктах м'якої матерії (скажімо у запорошеній плазмі), вивчається за допомогою геометричних методів (методу Вороного), а також у термінах відповідних параметрів порядку. Аналіз фазових діаграм у термінах орієнтаційного та трансляційного параметрів порядку показує, що структура гранульованих матеріалів є природно анізотропною. Ентропійна модель ґраткового газу застосована для опису вертикального профілю густини гранульованих матеріалів у зовнішньому гравітаційному полі. Отримані теоретичні результати добре узгоджуються із експериментальними даними, і майже точно відтворюють їх у найближчому околі станів з максимальним впакуванням.