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ENTROPY ANALYSIS FOR LOCAL STRUCTURE OF GRANULAR MATTER

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We apply phenomenological approach based on statistical mechanical concept in the form of Kirkwood-Buff arguments to describe the structural parameters of 2D binary granular mixture. By use of the scale-invariant model for radial distribution function first introduced in [1], we derive expression for correlational integrals which necessarily include geometrical parameters which characterize the properties of the local structure. In particular, expression for the packing fraction has been obtained analytically. We have also obtained the relation between macroscopic properties, such as entropy excess, and parameters of local structure, namely the packing fraction. Entropy excess and entropy difference for states spanning an interval of η = [0.8175 - 0.8380] has been performed and analyzed by means of contrast mapping. Calculations demonstrate non-monotonic behavior of the entropy excess and, in particular, shows presence of the minimum of S^{exc} at η= 0.8209. From the excess entropy difference we estimate the entropy production, associated with the transition between different configurational states with an individual local symmetries. Developed approach (because of the scale invariant character of the model measure of state) has been proposed for use with systems that have an isomorphic morphology of the local structure.

Keywords Granular matter, Local structure, Statistical mechanics, Entropy

1. INTRODUCTION

The study of local structure of granular materials (GM) and its transformations under the external perturbations has attracted a lot of attention over the last decades [2]. A variety of local arrangements have been observed in experimental and numerical studies including symmetric and asymmetric mechanically stable mono- and bi-disperse packings with different probabilities of occurrence. Understanding the influence of geometry of small clusters of particles (i.e. local structure) onto the properties of GM is one of the key issues in the study of static and dynamical properties of GM.

Of particular interest in the study of structural properties and dynamical behaviour of granular materials is the possibility of employing methods of statistical mechanics to describe these fully athermal, dissipative, nonlinear many-particle systems. However, despite recent achievements in this field, this possibility has not yet been adequately developed.

Difficulties in description of granular matter owe much to the lack of rigorous physical arguments (or properly specified constraints) on which a statistical description of the system can be based. We suggest that these abovementioned specific constraints be satisfied when outcoming energy flux (due to dissipative nature of GM) and incoming energy flux (implemented by external perturbation) are completely compensated.

The main difference between statistical systems and granular materials is that energy is no longer state variable, because of the non-equilibrium, dissipative and athermal nature of GM. There are a lot of attempts toward the incorporation of methods of statistical mechanics into the study of GM [3-5] based on the Edwards approach [6,7]. A key points in this approach is that the volume of the system is the analogue of system energy in equilibrium thermal systems, and entropy of the system must be the function of volume. In this respect, an open issue regards the possibility of determination macroscopic thermodynamic parameters (i.e. entropy or it's excess) as functions of local structure parameters. Previous works have proposed several different methods of entropy calculation [8]. It is important to stress, that conceptual issue in validating of the application of statistical mechanics methods in the description of granular matter involves probing their ergodicity under the different external conditions [9,10,12].

In this study, we present an extension of proposed earlier approach which employs Kirkwood-Buff [11] theory supplemented by incorporation of the model of radial distribution function (RDF) [1]. This approach permits us to derive analytical expression for the entropy excess S^{exc} in terms of parameters of local structure. We ask how the entropy excess and its difference change in the interval of packing fraction $\eta \in$ [0.8175 - 0.8380] i.e. in the vicinity of Random Close Packing (RCP) point, and then we find out the minimum of S^{exc} at η = 0.8209. The approach thus developed can also be effectively applied to quantify local structure of other objects of soft matter whose structure developed in meso- and macroscale.

2. KIRKWOOD-BUFF THEORY

Kirkwood-Buff (KB) theory, which is widely used as familiar theoretical tool in the studying liquid mixtures, relates macroscopic properties of systems (compressibility, entropy, etc) to the integrals of the radial distribution functions (RDF) G_{ij}

$$G_{ij} = \int_0^\infty (g_2(r) - 1) 4\pi R^2 dr . \quad (1)$$

In the case of GM, in which particles are large and could be observed by the naked eye, we have possibility to use approximation for RDF in form [1]

$$g_{ij}(r) = \Theta(r - d_0^{(ij)}) + A_{ij}\delta(r - d_1^{(ij)}) \quad (2)$$

where: r = |r1 - r2| ; r1 and r2 are the coordinates of the specified pair of particles; Θ (z) and δ (z) are the generalized Heaviside and Dirac functions, respectively. Parameter $d_0^{(ij)}$ may be considered as a diameter of a single particle (treated as a hard sphere). Model expression (2) describes a short - range order in the vicinity of selected particle. Parameter $d_1^{(ij)}$ = b $d_0^{(ij)}$ could be interpreted as the size of the first coordinate sphere or as characteristic lengthscale on which structural and dynamical heterogeneities take place. Application of scale-invariance model for RDF allows us to obtain analytical expression for correlational integrals G_{ij}, which for 3D system has the following form

$$G_{ij} = \frac{3}{4}\pi (d_0^{(ij)3} - d_1^{(ij)3} + 3A_{ij} d_1^{(ij)2}) \quad (3)$$

By introducing the normalization condition for RDF in form

$$\frac{1}{\widetilde{V}} \int_{\widetilde{V}} g_{ij}(r) dr = 1 \quad (4)$$

one can write coefficient A_{ij} in form

$$A_{ij} = \frac{\widetilde{V} - 8V_{ij}N}{4\pi N b^2 d_0^{(ij)2}} \quad (5)$$

here : $\widetilde{V}$ - is considered volume ; N - number of particles in $\widetilde{V}$; V_{ij} - volume of particles with diameter

$$d_0^{(ij)} = \frac{d_0^{(1)} + d_0^{(2)}}{2};$$

Substitution (5) into (3) gives rise

to $$G_{ij} = V_{ij}(2 - \eta_{ij} - 8b_{ij}^3) \quad (6)$$

where η_{ij} is packing fraction. For 2D case application of the appropriate normalization conditions leads to following expression for G_{ij}

$$G_{ij} = 2\pi\Omega_{ij} - \frac{1}{4} b^2 N_{ij} S_{ij} \quad (7)$$

here Ω_{ij} is square of local arrangement and $N_{ij}S_{ij}$ is square of all particles in given arrangement (See Fig. 1).

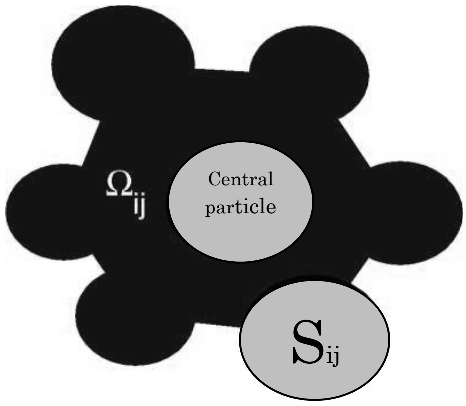

Fig. 1 - Sketch of the local arrangement of appropriate particles.

3. ENTROPY EXCESS

Phenomenological description of local structure and it's anomalies often performed by the studying the behavior of entropy excess. Such a study also provides necessary information about the stability of system and answers the question about the ability of system to be in specific point on phase diagram. The KB approach developed above can be used for description of entropy excess.

KB entropy excess S^{exc} in case of athermal mixture is defined as

$$S^{exc} = - \frac{k_B \rho \Delta_{12} x_2^2}{2} \quad (8)$$

where $\Delta_{12} = G_{11} + G_{22} - 2G_{12}$, $\rho = \frac{N_{12}}{\Omega_{12}}$ is number density, x_2 is partial concentration of second component and k_B is Boltzmann constant.

Then, substituting (7) into (8), one can rewrite entropy excess in terms of parameters of local structure as follows

$$S^{exc} = -\frac{k_B \rho x_2^2}{2} \text{ x } \Delta_{12} \qquad (9)$$

$$\Delta_{12} = 2\pi(\Omega_1 + \Omega_2 + 2\Omega_{12}) - \frac{b^2}{4}(N_2 S_2 + N_1 S_1 - 2N_{12}S_{12}) \cdot$$

Expression (9) necessarily includes parameters of local structure. Information about the local structure parameters in case of GM could be obtained directly from phenomenological information or with the help of numerical simulation.

One can see, that S^{exc} consits from two parts, the difference between which could be interpreted as corresponding dimensionless free volume on the local level. If we adopt, that $\omega_{ij} = \Omega_{ij} - N_{ij}S_{ij}$ is the portion of the free volume in local arrangement and $\frac{b^2}{4} = 2\pi$, then Eq.(9) directly demonstrates the influence of the excluded volume onto the entropy excess of local arrangement. By definition entropy excess S^{exc} reads as

$$S_k^{exc} = S_{m,k} - S_{id}$$

where $S_{m,k}$ is a measured value of entropy at given state and S_{id} is a value which is defined for ideal reference state (definition of which is a separate task). Thus, one can derive entropy excess difference ΔS_{kl}^{exc} between two states k and l as

$$\Delta S_{kl}^{exc} = S_k^{exc} - S_l^{exc} = S_{m,k} - S_{m,l} \,.$$

Thus entropy difference could be written as

$$S_{m,k} - S_{m,l} = -2k_B N_{12} x^2 \pi(\eta_k - \eta_l)$$

where η is a packing fraction of given state. Obtained relation permits to derive entropy production $\frac{S_{m,k} - S_{m,l}}{\eta_k - \eta_l} = -2k_B N_{12} x^2$ due to compactization. By use Eq.(9) we quantify different states which were observed in the experimental study [13]. We focus on a local arrangement of particles which consists of central one and its neighbours. We consider only stroboscopic snapshot at the moment when system reaches steady state. On Fig. 2 we capture values of entropy excess for each particle configurated for states with slightly different values of packing fraction η.

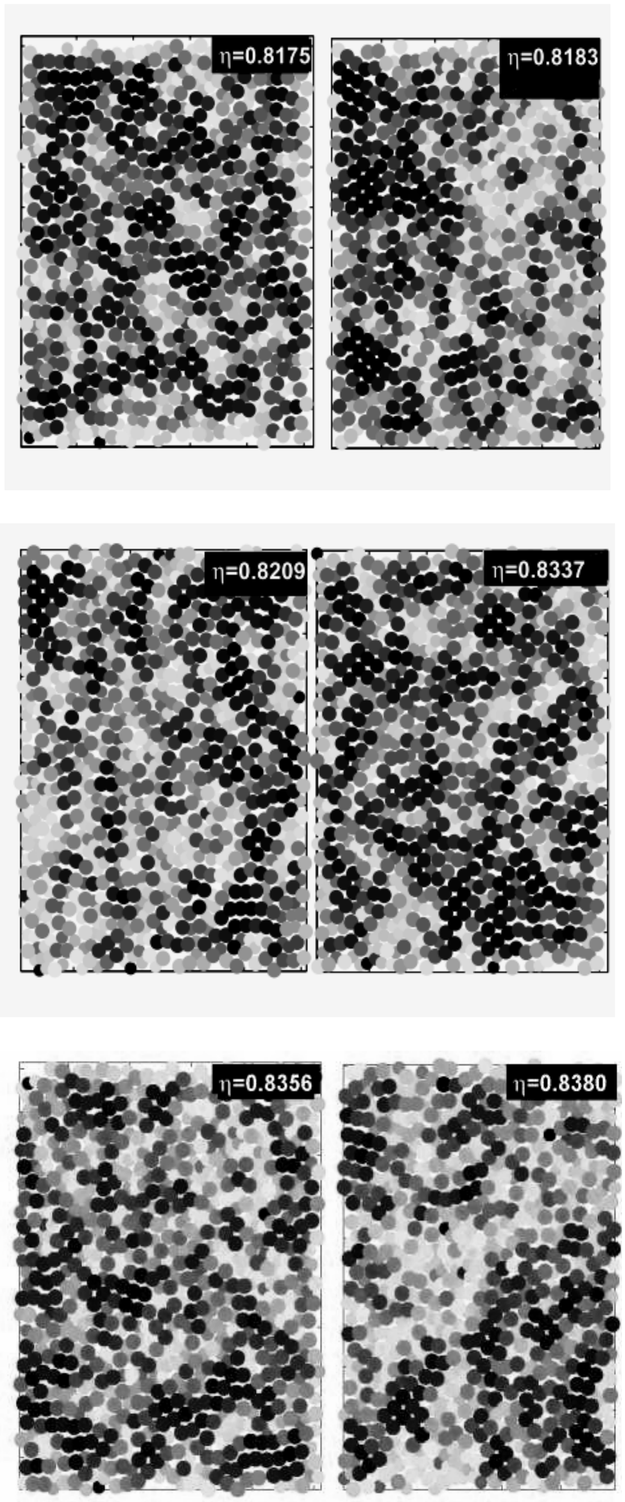

Fig. 2 - Entropy excess S^{exc} per particle for sequence of states observed in experimental study [13]. Particles are contrasted according to their entropy excess values.

Fig. 3 shows the behavior of the mean entropy excess S^{exc} with localization of extremum at $\eta = 0.8209$.

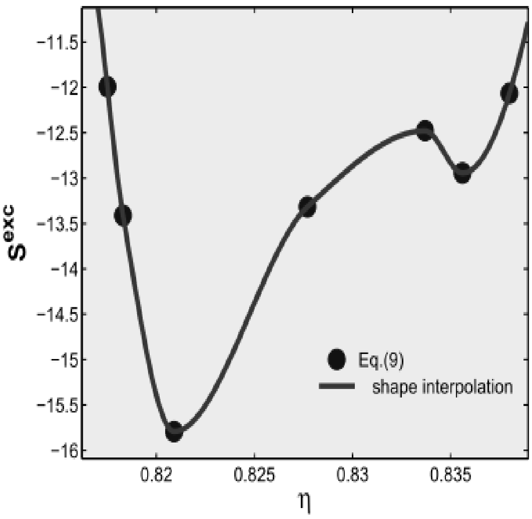

Fig. 3 - Mean value of entropy excess Sexc versus packing fraction η for sequence of states observed in experimental study performed in [13].

Fig. 4 displays an estimation of the entropy difference due to possible transitions between differently configurated states in the close vicinity of RCP.

4. CONCLUSIONS

In this work we have studied the structure of 2D binary granular materials with help of phenomenological approach supplemented by certain statistical-mechanical argumentation. Being based on scale-invariant direct analytical model for RDF [1], adopted KB approach allows us to construct the relevant expression for entropy excess S^{exc} related to a single particle.

Further, we define a measure of the mean entropy excess and its change due to compactisation, and find that in the interval of $\eta \in$ [0.8175-0.838] there is an extremum of entropy excess S^{exc}. In some related papers entropy analysis has been done by alternative methods and directed to GM with a different levels of compactisation(see ,for instance [6,7,10]).

The presence of a minimum in S^{exc} at $\eta = 0.8209$ could possibly be explained by existence of some intermediate metastable local states which happens due to configurational rearrangements in binary mixtures. Therefore the entropy excess analysis permit us to analyze the strucuure of densily compacted GM in more details. Due to scale invariance of model for RDF, the entropy defined in this paper offers the way to investigate the entropy difference (excess) associated with local structures transformations in wide class of objects of the soft matter. Also we would like to note that it could be interesting to compare obtained results with entropy analysis done by means of,say, Voronoy tesselations applied to isomorphic systems. This would be realised in our next paper.

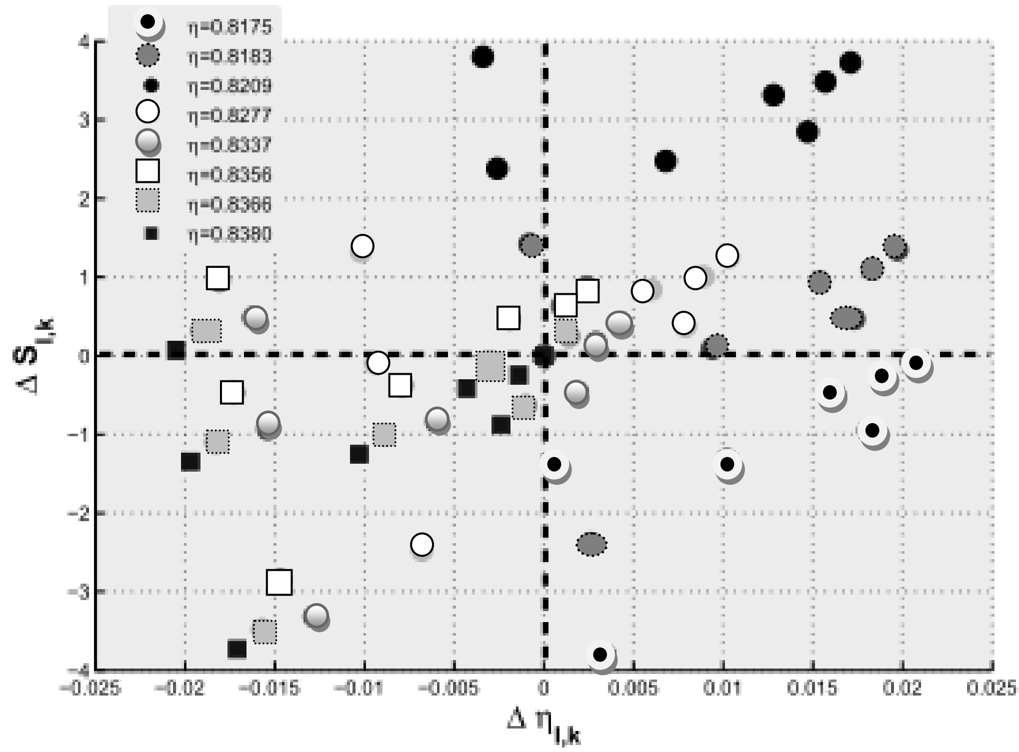

Fig. 4 - Estimation of the entropy difference due to possible transitions between differently configurated states in the vicinity of RCP.

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ЕНТРОПІЙНИЙ АНАЛІЗ ЛОКАЛЬНОЇ СТРУКТУРИ ГРАНУЛЬОВАНОЇ МАТЕРІЇ

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Феноменологічний підхід розвинутий в роботах Кірквуда-Баффа застосовується для опису параметрів локальної структури та опису переходів між різними за симетрією станами в бінарних гранульованих матеріалах. Використання аналітичної моделі для парної функції розподілу,введеної в [1] дозволило отримати аналітичні вирази для надлишку ентропії та її змін внаслідок структуризації. Аналітичний аналіз та відповідні чисельні розрахунки дозволили встановити значення параметру впакування в околі якого відбуваються структурні перетворення гранульованих матеріалів. Отримані результати добре корелюють із даними безпосередніх фізичних експериментів.

Ключові слова: гранульована матерія, локальна структура, статистична механіка, ентропія

ЭНТРОПИЙНЫЙ АНАЛИЗ ЛОКАЛЬНОЙ СТРУКТУРИ ГРАНУЛИРОВАННОЙ МАТЕРИИ

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Феноменологический подход развитый в работах Кирквуда-Баффа используется для описания параметров локальной структуры и переходов между различными по симметрии состояниями в бинарных гранулированных материалах. Использование аналитической модели для парной функции распределения введенной в [1] позволило получить аналитические выражения для избыточной энтропии и ее изменений вследствие структуризации. Аналитический анализ и соответствующие численные расчеты позволили установить значения параметра упаковки в окрестности которого происходят структурные изменения в гранулированных материалах. Полученные результаты хорошо согласуются с данными непосредственных физических экспериментов.

Ключевые слова: гранулированная материя, локальная структура, статистическая механика, єнтропия

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