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Dear Editor,

E05064/Blumenfeld - response to referee reports

Thank you for the reports on the above manuscript. The first referee finds the work interesting but wants (i) to see an explicit calculation of the entropy and (ii) to clarify the relation between the fabric tensor and the entropy. The second referee also comments about the lack of explicit calculations of the entropy in three dimensions. Nevertheless, she/he finds the work interesting and recommends to publish after modifications that meet several specific comments. The third referee is critical and is concerned with two main issues: (i) the usefulness of the entropic analysis for cellular systems in general; (ii) the absence of an explicit calculation of the entropy. Both the second and the third referees suggest to replace the term Quark, adopted for an elementary volume, by another term. Both these referees also complain about problems with the figures and mathematical symbols, suggesting that they may have received a corrupt version of the manuscript.

In our response we try to follow the order by which issues have been raised in the reports. The main points of our response can be summarised as follows.
(a) We clarify the relation between the geometric tensor and the entropic formalism - the former provides the variables for the volume function in the partition function;
(b) we give two exact calculations of the entropy in three dimensions for idealised systems;
(c) we clarify the usefulness and applicability of the entropic approach for cellular systems both as a characterisation method and as a basis for connecting between structural and physical properties, such as permeability and conductivity in porous media, and therefore argue that it has at least the same validity as for granular systems, for which the 2nd referee admits the approach could be useful;
(d) we clarify several issues concerning boundary effects and the counting of the degrees of freedom;

(e) we replace the term 'Quark' by 'Quadron'.

Report 1:

Thank you for the supportive report. **(i)** We emphasise that the formalism published for granular systems in reference 4 was specific to two-dimensional systems. As we make clear in the introduction, the two-dimensional case is presented both for adaptation to cellular systems in general and for forming a basis for the formulation of the three-dimensional case. The three-dimensional "algorithm" discussed is new and has never appeared before.
(ii) To meet the referee's first request, we have included two explicit calculations of the entropy for three-dimensional cellular structures. One calculation is for an idealised Gaussian density of states and the other is inspired by cell size distributions in polymer foams. Please see more details in our response (v) to referee 2.
(iii) The relation between the fabric tensor and the entropy is given in the paper only for two-dimensional systems and is as follows. The fabric tensor, $\hat{C}_v$, provides a general characterisation of the local structure. From this tensor we extract the volumes of the quadrons, $A_{cv} \equiv A_q$. The volumes of the quadrons are the basic variables of the volume function $\mathcal{W}_2$, defined in eq. (3) (for three dimensions the construction of the quadrons is illustrated in figure 4). The volume function enters the partition function in the role of a Hamiltonian. From the partition function the entropy is computed. All this is now made clearer in the introduction and in the text starting from just before eq. (2) and ending just below eq. (3).
(iv) We are not sure why figures 1 and 2 are the same in the version that the referee received. In the copy that we have, which we believe is also the one we have sent, the figures are different and properly ordered.

Report 2:

Thank you for finding the work interesting and for the comprehensive and constructive comments.
(i) We are not sure why there is a problem with figure 1, we can only reiterate our response to referee 1 that in the copy we have, which we believe is also the one we have sent, the figures are fine. The same goes for the mangled text and symbols that the referee received.
(ii) The second parenthesis should read $(2r_2 + r_1)$. Typos corrected.
(iii) In light of the objection raised by two of the referees to the term Quark we have renamed these elementary units of the system quadrons. The term 'prototile' suggested by the referee is only apprpriate in two dimensions since in three dimensions the elementary units fill the space rather than tile it.
(iv) "In two dimensions, the tiles are obtained cleverly ([7] and [4]) in two steps...The three-dimensional case is particularly interesting...". Thank you!
(v) The comment about the title is related to the absence of explicit calculations of the entropy. We have now included such calculations both in two and in three dimensions and so we would rather keep the title as is. Because of the novelty of the method of characterisation there is no direct data on the

statistics of the quadron volumes. To demonstrate the use of the formalism, we then have to give examples of possible density of states Θ. For completeness, we have analysed several possibilities in two dimensions and we could do the same in three dimensions, but this would only be repetitive. Therefore, in the modified version we present only two illustrative three-dimensional cases. It should be remembered that the caluculations are intended to illustrate the method, not as a solution of a particular physical system. Nevertheless, one of our examples is inspired by data on cell size distributions in polymer foams (see the new reference 12). The other three-dimensional example is for an idealised Gaussian density of states. The calculations are presented starting on page 11. We have included a brief discussuion of this approximation in the concluding section starting on page 12. We have also included explicit calculation of the entropy for the first two-dimensional example system (the second of eqs. (7) and outlined the derivation of it in the other two examples in two dimensions and the following two examples .

(vi) Regarding the footnote, according to the format of EPJE the acknowledgement comes at the bottom of the first page. We have used the standard EPJE template.

(vii) We have re-worded the sentence containing the repetitive phrase, it now reads "Relying on observations that under specified vibrations granular assemblies settle into packings of reproducible densities, it was proposed that there is a steady state distribution of configurations." (page 2, column 1, 11 lines from bottom)

(viii) The question whether the ensemble is canonical or microcanonical depends on whether the volumes of its members are fixed (the latter) or allowed to change (the former). In other words, whether the volume function adds up to a constant across the entire ensemble or not. This issue is not crucial for the formalism presented in the manuscript. Nevertheless, we accept the possible implication that ensembles of systems with fluctuating volumes could be of more immediate interest to experiments and we have modified the discussion to relate to canonical systems. We have added a comment to clarify this issue (page 3, column 1, 7 lines from bottom).

(ix) As mentioned in the manuscript, the term 'free volume' has a specific association in the community and using this term with a different meaning here could be confusing. The relevance of the analysis to porous media prompted the use of 'free porosity' which we would rather stick to. The mean volume is now redefined as the volume (of the cells or bubbles) per quadron.

(x) Reference 5 to Euler has been deleted and references to Wearie/Rivier and Coxeter added, as suggested. (page 3, section 2, line 2 from bottom)

(xi) Thank you for the comment regarding the effect of the boundary. In the manuscript we have bounded this effect by estimating it to be of order $1/\sqrt{N}$ and hence argued that it is negligible. However, we did not make it sufficiently clear that this is an *upper bound*. The referee suggests another argument that may give a better bound. Nevertheless, this argument is not immediate and it would require a detailed discussion, not the least because the number of edges of the extra cell in S_D would also be of order $\sqrt{N}$. Since the refining of the upper

bound on the correction is downstream from the main discussion anyway, we are not bothered by the roughness of our estimate and prefer it in order to keep the paper as clear as possible. We now clarify in the text that the correction is at most of order $1/\sqrt{N}$. (page 3, section 2, line 13)

(xii) The fabric tensor described in eq. (2) has been introduced for the first time in reference 7 for granular systems. It was used for analyses of stresses in cellular structures for the first time in reference 6. We therefore do not see how these references can be extended.

(xiii) The caption of figure 2 has been modified to lift the confusion pointed out by the referee. We have also marked the centroid of the cell bt X to make the definition of clearer.

(xiv) We are puzzled by the referee's comment regarding the "surprising coincidence". First, the referee writes "In 2D, each cell constitutes an independent circuit.thus 3N/2 thereof." There are only N/2 cells! There are 3N/2 'independent' circuits altogether (these are the irreducible loops that we discuss in the paper) but the extra N circuits come from the triangles around the vertices. Second, the referee says that each edge gives one Quadron, hence 3N Quadrons altogether. However, the issue is to show that this number is the same as the number of independent degrees of freedom and this equality does not follow from her/his argument. In particular, we do not see how would one conclude from the 3N/2 "independent circuits" that there are 3N independent degrees of freedom in the volume function?

What we have done is to count the number of independent degrees of freedom as follows. We first used our construction of every edge as a vector to identify the total number of variables - two vector components per edge and therefore 6N variables altogether. We then used the fact that each of the 3N/2 irreducible loop has exactly one dependent vector, namely, two dependent variables. Thus, $6N - 2 * (3N/2) = 3N$ is the total number of (independent) degrees of freedom, exactly as the number of Quadrons. The reason that we refered to it as a surprise is that this equality seems to be unique to two dimensions and has no analogue in three dimensions, as we discuss in the text.

(xv) 'Quarks' has been replaced by 'Quadrons'.

(xvi) Vectors $\vec{a}$ and $\vec{b}$ are in fact $\vec{r_1}$ and $\vec{r_2}$. Typos corrected.

(xvii) We have modified the description of the cell surface in a way that obviates the use of the planetarium concept. (page 8, column 1, line 14)

(xviii) We accept that "triangular network" has a common meaning in the community, which is not the one we intended. We meant to describe a network of triangles that comprises of interconnected triangles which enclose polygons. We have now replaced this term by "a network of triangles", which we believe is free of that association. (page 8, column 1, line 18)

Report 3:

(i) "At the heart of the paper is the question of whether the proposed description of the degrees of freedom of such systems is useful. I think that this has not been established."

Concerning usefulness, we point out that prior to our proposed description only

approximate volume functions have been used in the literature. The degrees of freedom that we propose make it possible, for the first time, to construct *exact* volume functions in two and in three dimensions. The significance of this cannot be overemphasised in view of the fact that volume functions are used as Hamiltonians and the volumes are the analogues of particle energies in conventional statistical mechanics. Thus, for the large community that works on foams and cellular structures it is surely preferable to analyse the entropy with exact, rather than approximate, volume functions. Regarding the applicability of the method, see our responses below.

(ii) "...the applicability of the Edwards thermodynamic approach to such structures (save granular materials, for which it was devised, and even there is controversial) is less than not established, it has not even been proposed. Thinking about it, one would be very surprised indeed if a thermodynamic approach could be at all relevant to foams in any dimension. "

This comment involves several issues. First, we point out that an ever growing community in granular materials regards the Edwards approach as both having been established and useful. A sample of the many relevant references is Jaeger and Nagel, Rev. Mod. Phys. 68, 1259 (1996); Kruyt and Rothenburg, Int. J. Solids Struct. 39, 571 (2002); Nicodemi, Phys. Rev. Lett. 82, 3734 (1999); Makse and Kurchan, Nature 415, 614 (2002); Metzger, Phys. Rev. E 70, 051303 (2004).

Second, the concept of entropy in foams and cellular systems is not our invention. It has been introduced already in the mid eighties to compute various structural properties of foams as well as in an attempt to use maximum entropy production as a guideline for the modelling of the dynamics of evolving foams. There are many works that we could refer the referee to. Selected examples are, Rivier, Philos. Mag. B. 52, 795 (1985); Peshkin, Strandburg, and Rivier, Phys. Rev. Lett. 67, 1803 (1991); Iglesias and de Almeida, Phys. Rev. A 43, 2763 (1991); Stavans, Rep. Prog. Phys. 56, 733 (1993), as well as our reference 2. We have simply extended the idea to describe structures where the physical temperature is not important by adapting the compactivity concept.

Third, the key observation that makes a statistical mechanical approach applicable to foams and to cellular structures is that these systems usually converge into a steady-state scaling regime where the distributions of the structural properties are constant when the space dimension is scaled by an appropriate power of time, $r \to r' = r/t^x$. This phenomenon has been observed in many experiments and simulations and it is explicitly discussed in almost all the references mentioned in the previous paragraph. Thus, although foams are not in thermal equilibrium, the existence of a steady state makes it possible to use this to calculate various expectation values. This is the same logic that led to the use of statistical mechanical tools to granular systems following oservations of steady state distributions of granular assemblies under particular vibrating conditions. In fact, the steady state in foams is usually more robust and less sensitive to specific organisation dynamics than in granular systems. Thus, the applicability of a statistical mechanical analysis to foams should be at least as valid as for granular systems. All this is now clarified in the introduction. (page 2, column

2, paragraph beginning with "In cellular systems...")
Fourth, our formalism, which is based on the new degrees of freedom, achieves two main goals: (a) it provides a general method to characterise arbitrary cellular structures (i.e. by the fabric tensor in two dimensions, which can be readily extended to three dimensions, an exercise we have not done in full detail because, in our view, it is directly relevant to the thrust of this paper, which is the introduction of our entropic formalism), and (b) it makes it possible to compute the expectation value of *any* structural property.
Moreover, in view of the latter applicability, it has been proposed recently that entropic characterisation can be further used to make progress on the old problems of structure-permeability and structure-brine conductivity relations in porous media (see awarded EPSRC grant GR/T28959/01,
http://www.poco.phy.cam.ac.uk/ rbb11/EPSRCGrT2895901.mht). Thus, there is ample evidence that entropic characterisation in general, and our formalism in particular, is useful to the fields of foams, porous media, and the plethora of cellular materials.
(iii) "...the applicability of the Edwards thermodynamic approach ... has not even been proposed." Indeed this is the first time that a statistical mechanical approach based on the concept of compactivity has been proposed for cellular systems. Surely, the introduction of a novel idea is an advantage when considering a manuscript for publication rather than a disdvantage.
(iv) "...nor has the entropy been explicitly performed as the title suggests. ... the calculation of the entropy of the 3D systems treated is certainly not immediate, if possible at all."
The referee repeats this comment several times in various forms throughout the review. The absence of explicit calculations of the entropy, both in two and in three dimensions has been rectified. In three dimensions we have included two calculations of the entropy for idealised systems. As the referee requested, one of these examples is inspired by data from a physical system - the cell size distribution in polymer foams (see reference 12). Please see more detail in our response (v) to referee 2. This also answers the referee's concern whether such a claculation is possible at all.
(v) "This is seen in the fact that the number of degrees of freedom is smaller than the number of of "quarks"".
The fact that the number of independent degrees of freedom in three dimensions is smaller than the number of Quadrons does not hinder the calculation of the entropy nor does it bear on the validity of the approach. It only highlights the fact that there are correlations between these unit volumes and therefore that in general they should not be considered as the independent degrees of freedom that span the phase space. The reason for the indeterminacy of the exact number of degrees of freedom can be traced directly to the indeterminacy of the Euler relation. Therefore, we can only bound or approximate the phase space. The three-dimensional calculation presented in the modified text is carried out using in principle the exact number of degrees of freedom and leaving it as an unknown parameter for the extensive quantities. By calculating expectation values per Quadron the quantities become intensive and this pa-

rameter disappears. Thus, by neglecting inter-Quadron correlations altogether this then becomes an 'ideal gas approximation'. It is significant to note that the correlations between the variables that one uses in the partition function do not invalidate the approach - this only highlights the lack of accurate knowledge about the state of the system.
We remind the referee that approximations of the number of degrees of freedom, when it is not exactly known, are not new in statistical mechanics. For example, in systems of macroscopic bodies. Although the bodies are made of many molecules whose positions and momenta should go in principle into the partition function, because of the strong correlations between molecules within any one body it is approximated as one particle. For integration purposes then, the phase space consists of only the positions and momenta of the centres of mass of the macroscopic particles. In this example, the fact that one has to approximate the number of 'frozen' degrees of freedom, has no bearing on whether the use of a partition function is valid (it depends mainly on the nature of the steady-state distribution of states).
(vi) "That simulations or experiments must be invoked to measure the probability density ... means that the results of the paper are, by themselves, not very illuminating...".
This is a puzzling statement. In traditional statistical mechanics, the validity and usefulness of a partition function is independent of whether we know how to calculate the statistics of the variables that appear in the Hamiltonian or the exact density of states. There are two ways to arrive at such data: either to assume a model, e.g. ideal gas, Bose-Einstein statistics, Fermi-Dirac etc., or to measure experimentally the density of states, e.g. the distribution of photon frequencies in a black box. Our paper describes exactly the same situation - there is a formalism based on a partition function, an entropy, and a volume function. To find the equivalent of the density of states (i.e. $\Theta(\{V_q\})$) we may either measure a particular ensemble of configurations (experimentally or numerically) or we may assume a particular statistics. In the absence of data on the statistics of Quadron volumes we have chosen to follow the latter route. This is one step removed from the formalism, its usefulness, or even the possibility of an explicit calculation, which we demonstrated to be able to do.
(vii) The term 'Quarks' has been replaced by 'Quadrons' which does not have prior associations.

In conclusion, we believe that this response addresses fully and convincingly all the comments of the referees. We have modified the manuscript following the referees' comments as we have outlined above. Enclosed please find a PDF file containing the new version. We look forward to hearing from you.

Yours sincerely,

Dr. Raphael Blumenfeld Prof. Sir Sam F. Edwards