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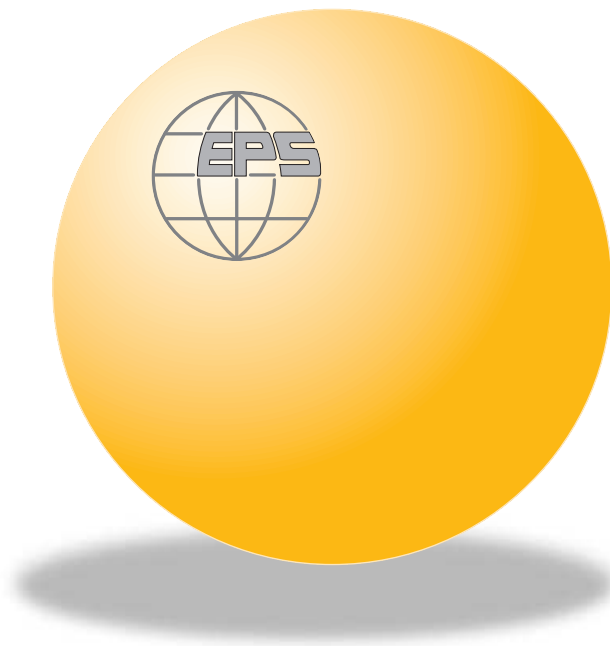
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**Cell theory for liquid solids and glasses:
From local packing configurations
to global complex behaviors**

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T. ASTE and A. CONIGLIO



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Cell theory for liquid solids and glasses: From local packing configurations to global complex behaviors

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Abstract. – We develop a novel approach that combines the ideas of inherent structures, free-volume theory and geometrical packing properties to derive a general theory to understanding the complex dynamics of glass-forming liquids, granular packings and amorphous solids. We show that the thermodynamical properties of these systems can be retrieved from the study of geometrical and topological properties of local configurations only. When applied to hard-sphere systems, the present theory describes the critical approach toward the random close-packing density with the configurational entropy that approaches zero, and the α -relaxation time that diverges according to the Vogel-Fulcher behavior following also the Adam-Gibbs relation. The equation of state derived for the stable fluid, the metastable fluid, and for the crystalline and amorphous solids, results in good quantitative agreement with the data available in the literature.

In the context of glasses there are many valuable theories based on free volume [1], cooperative rearrangements of particles [2], inherent-structures approach [3–5], mode coupling theory [6], replica theory [7]. We develop a novel approach (which combines some of the features of free-volume and the inherent-structures approach) that can be applied to a broad variety of systems: from foams to van der Waals systems, from granular packings to colloid suspensions. In this paper we discuss in detail the case of identical hard spheres, which is a good model-system for granular media and has been widely studied in order to have insights on the intrinsic structure of solids, liquids and glasses, to investigate biological tissues, to understand the bare nature of disorder [8–10]. For this system, we retrieve quantitatively the equation of state, we describe the transition between fluid to amorphous solid and crystalline solid phases, the occurrence of a critical behavior toward maximal compaction with large relaxation times which diverge in agreement with both the Adam-Gibbs and Vogel-Tammann-Fulcher equations and the configurational entropy that approaches zero.

We write the configurational partition function Q for N undistinguishable particles in a volume V as a sum over the contributions associated to a set of states “ α ”. These states are

packing configurations $\{\mathbf{r}_1^\alpha, \dots, \mathbf{r}_N^\alpha\}$ (points in the $3N$ -dimensional configuration space) associated to local minima of the energy $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ (inherent states [3]) or —more generally— they correspond to configurations where the probability to find the particles is locally a maximum:

$$Q = \sum_{\alpha} e^{-\beta F^\alpha} = \sum_{\alpha} \frac{1}{N! \Lambda^{3N}} \int d\mathbf{r}_1 \dots \int_{\mathcal{B}^\alpha} d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)}, \quad (1)$$

where $\Lambda = h/(2\pi m k_B T)^{1/2}$ and $\beta = (k_B T)^{-1}$, with T the temperature, m the particle mass. The integral in eq. (1) is over the regions \mathcal{B}^α (volumes in the configuration space defined around the states $\{\mathbf{r}_1^\alpha, \dots, \mathbf{r}_N^\alpha\}$). Note that, if these regions \mathcal{B}^α do not overlap and if the $3N$ -dimensional configuration space is entirely tiled by the set of \mathcal{B}^α , then eq. (1) is an *exact* way to write the configurational integral.

For a given state α , we divide the volume V into N cells $C_1^\alpha, \dots, C_N^\alpha$ constructed around the positions $\mathbf{r}_1^\alpha, \dots, \mathbf{r}_N^\alpha$. In this way we associate to each state α a space partition. Each cell C_i^α is characterized by a set of parameters \mathbf{n}_i^α which carry the complete information about its geometrical and topological properties (size, shape, ...). The volume of cell C_i^α is $v(\mathbf{n}_i^\alpha) = \int_{C_i^\alpha} 1 d\mathbf{r}$ and the total volume is $V = \sum_i v(\mathbf{n}_i^\alpha)$. The configurational integral in eq. (1) is over the accessible packing configurations associated with each state α . In each configuration, the number of particles in a given cell can vary —in principle— between $m_i = 0$ to N (with the constraint $\sum_i m_i = N$). But, these cells are constructed around special positions that maximize the probability to find one particle in that region. Therefore, we expect that the configurations with the cells singly occupied would maximally contribute to F^α . We find that, for two-body interactions and under an Hartree-like approximation (see [11] and [12]), the expression for F^α can be written in terms of the local properties of the cells C_i^α :

$$F^\alpha \simeq \sum_i \epsilon(\mathbf{n}_i^\alpha) - k_B T \left[\ln \frac{u(\mathbf{n}_i^\alpha)}{\Lambda^3} - \ln \mathcal{P}(\mathbf{n}_i^\alpha) \right], \quad (2)$$

with $\epsilon(\mathbf{n}_i^\alpha)$ the energy contribution from a particle in the cell C_i^α , $u(\mathbf{n}_i^\alpha)$ the “free volume” [11,13,14] associated with the cell C_i^α and with $\mathcal{P}(\mathbf{n}_i^\alpha)$ the probability of finding cell “ i ” singly occupied. In the literature there are different definitions of “free volume”. In the present case, consistently with [11], the free volume —for hard spheres— is the volume within a distance $d/2$ from the cell boundaries (see [15]). With eq. (2) we have now reduced the expression for the free energy to a sum over the contributions from each cell “ i ” which is fully characterized by its geometrical and topological parameters \mathbf{n}_i^α . As a consequence, the expression for the free energy can be written as a function of the distribution of the cell shapes and sizes: $F^\alpha = F(\{N^\alpha(\mathbf{n})\})$, with $N^\alpha(\mathbf{n})$ the number of cells characterized by the set of geometrical and topological parameters \mathbf{n} . Different α are associated with distinct cellular partitions, therefore the sum over the states α in eq. (1) can be substituted with a sum over the space partitions $\{N^\alpha(\mathbf{n})\}$ associated with these states, leading to

$$Q = \sum_{\alpha} e^{-\beta F(\{N^\alpha(\mathbf{n})\})} = \sum_{\{N(\mathbf{n})\}} \Omega(\{N(\mathbf{n})\}) e^{-\beta F(\{N(\mathbf{n})\})}, \quad (3)$$

where $\Omega(\{N(\mathbf{n})\})$ counts the number of distinct space partitions made with the set $\{N(\mathbf{n})\}$. For instance, all such cells are identical in an FCC crystalline packing (rhombic dodecahedra) and in this case $\Omega = 1$. On the other hand, the cells from inherent states associated with non-crystalline structures have, in general, different shapes and volumes. A classification in terms of their topologies and volumes can be found in [16] for hard spheres and in [17] for Lennard-Jones systems. This quantity cannot be evaluated in general but we can calculate its maximum

value. Indeed, the maximum number of distinct configurations that can be made by positioning in different ways N cells distributed in groups of $N(\mathbf{n})$ is: $\Omega(\{N(\mathbf{n})\}) \leq N! / \prod_{\mathbf{n}} N(\mathbf{n})!$. This maximal value cannot be in general achieved since some of these combinations do not generate space-filling assemblies and others might not correspond to any state α or might be associated with overlapping regions of the configuration space. However, we can assume that the total number of distinct configurations can be *approximated* by this quantity. Since the total number of distinct configurations correspond to the total number of minima of the potential energy, we have that the configurational entropy per particle is given by $s_c = \frac{\ln \Omega}{N}$.

We now introduce a saddle-point approximation where the sum over all the distributions in eq. (3) is replaced with the contribution from the distribution $N^*(\mathbf{n})$ which maximally contributes to Q . We obtain

$$\frac{\ln Q}{N} = -\beta \sum_{\mathbf{n}} \frac{N^*(\mathbf{n})}{N} \left[\epsilon(\mathbf{n}) - k_B T \left(\ln \frac{u(\mathbf{n})}{\Lambda^3 \mathcal{P}(\mathbf{n})} - \ln \frac{N^*(\mathbf{n})}{N} \right) \right], \quad (4)$$

with the saddle-point distribution $N^*(\mathbf{n})$ given by

$$\frac{N^*(\mathbf{n})}{N} = \frac{u(\mathbf{n})}{\Lambda^3 \mathcal{P}(\mathbf{n})} \exp [-\beta \epsilon(\mathbf{n}) - \theta v(\mathbf{n}) - \lambda], \quad (5)$$

where the two coefficients θ and λ are Lagrange multipliers which are fixed by the two constraints: $\sum_{\mathbf{n}} N^*(\mathbf{n}) = N$ and $\sum_{\mathbf{n}} v(\mathbf{n}) N^*(\mathbf{n}) = V$. In practice, we generate a large set of cells. Then, varying θ , we obtain the cell distribution from eq. (5) and, consequently, the density as a function of θ . All the calculations are made as a function of θ , which in turn can be expressed as a function of the density. At any given density, eq. (5) gives the distribution of cell shapes and sizes that minimizes the system free energy. The cell shapes are given by the underlying inherent state, whereas the cell sizes are changed in order to match the given overall density. Therefore, in order to calculate the dynamical properties of the system we must first investigate a set of attainable cell shapes associated with the inherent states. Then eq. (5) gives us their combinations in numbers and sizes that maximally contribute to the partition function.

This result (eqs. (4), (5)) applies to a broad class of systems with different interactions and different particle sizes and shapes. In one dimension, eqs. (4), (5) can be calculated analytically yielding to the exact expression for Q . We now study in detail a simple three-dimensional case where the particles are hard spheres with equal diameters d . One of the most relevant parameters in these systems is the packing density (ρ) that is the fraction between the volume occupied by the balls divided by the total volume. It is known that the maximum density attainable in a packing of equal balls is $\rho = \pi/\sqrt{18} = 0.7404\dots$. This limit cannot be attained in disordered packings where maximal densities around 0.64 are generally found [9, 10, 18]. There are many studies on the nature of the hard-sphere glass transitions [16, 19–23]. Experiments on colloidal systems seem to indicate a structural arrest close to a value $\rho = 0.57$ [24, 25]. This transition is characterized by power law divergence in the large relaxation time and can be well described in terms of the mode coupling theory [26]. However, other experiments on colloidal systems [27] show that the approach toward the maximal disordered density is critical with the viscosity that grows exponentially fast (Vogel-Tammann-Fulcher behavior) following the Adam and Gibbs relation. Hereafter we apply the present theory to a system of hard spheres. We derive the equation of state for both the glass and the crystal, and show that the large relaxation time follows the Vogel-Tammann-Fulcher behavior, and satisfies the Adam Gibbs relation.

The thermodynamical properties of the system can be determined, through eqs. (4) and (5), by analyzing the set of attainable local packing configurations and calculating the associated quantities $v(\mathbf{n})$, $u(\mathbf{n})$, $\mathcal{P}(\mathbf{n})$ ($\epsilon(\mathbf{n}) = 0$ for hard spheres). To this end, let us identify the cell C_i^α , with the Voronoi cell (also known as Wigner-Seitz cell or Dirichlet region) [28] generated by bi-setting with planes the segments between the centre of sphere “ i ” and the centres of its neighboring spheres. The free volume associated with such a cell is the volume of a smaller cell generated from C_i^α by moving the faces normally inside of a distance $d/2$ [14, 15]. In this Voronoi construction, the geometrical and topological properties (\mathbf{n}_i^α) of a cell C_i^α are fully given by the set of vectors $\mathbf{e}_{i,j}$ between the positions of the central sphere and its surrounding ones. We explore the configuration space by generating a large number of local packing configurations placing n hard spheres around a central one at positions $\mathbf{e}_{0,1}, \dots, \mathbf{e}_{0,n}$. We first explore the possible shapes of these Voronoi cells by generating compact local configurations, then we produce larger cells by performing a uniform radial expansion. The compact local configurations are generated by placing (avoiding overlaps) the surrounding spheres at random positions with radial distances in the range $d \leq |e_{0,i}| \leq 1.05d$ [29]. Here, the coefficient 1.05 is a measure of the *geometrical frustration* [30]. The reasoning which leads to this value is the following: the densest local packing configuration is made with 12 spheres placed at radial distances $h = d$ on the vertices of an icosahedron. But, this configuration cannot tile space without leaving larger gaps. Indeed, the surrounding spheres are not in contact with each other but stay apart at a distance $h' = \sqrt{8/(5 + 5^{1/2})}d \simeq 1.05d$. Consistently, we assume that in the closest packings the distances between neighboring spheres stay at least in a range between d and $1.05d$. We generate more than 10^7 of such configurations with one central sphere and a number of neighboring spheres between $4 \leq n \leq 16$. For each configuration we evaluate: i) the volume $v(\mathbf{n}_i)$ of the Voronoi cell; ii) the free volume $u(\mathbf{n}_i)$; iii) the caging probability $\mathcal{P}(\mathbf{n}_i)$. This last quantity is fixed equal to 1 if the n external spheres are placed in such a way to prevent the internal one to move outside the cell (without displacing the external spheres or overlapping). Vice versa, to $\mathcal{P}(\mathbf{n}_i)$ is associated the value $1/e$ if the internal sphere is “free” to leave the cell. It must be pointed out that the identification of this geometrical quantity with the probability of single occupancy is a reasonable but unjustified assumption. We must, however, note that the choice of \mathcal{P} affects very marginally the results for the equation of state and the free energy. Once $v(\mathbf{n}_i)$, $u(\mathbf{n}_i)$ and $\mathcal{P}(\mathbf{n}_i)$ are obtained, from eqs. (4) and (5), we compute the evolution of the statistical and thermodynamical properties of the system at different densities (*i.e.* for several θ).

In order to compare quantitatively the outcomes of the present theory with the data from numerical simulations for hard spheres [19, 22, 23], we use the thermodynamical relation $P = k_B T (\partial \ln Q / \partial V)_{N,T}$ to calculate $\frac{PV}{NkT}$ as a function of the density ρ (the equation of state). As shown in fig. 1a, we find a remarkable agreement between the theoretical prediction and the numerical simulation data. From fig. 1 we observe the separation into two branches for densities above ~ 0.5 . One branch corresponds to the disordered glassy state, and the other is associated with the ordered-crystalline structure. So far, we have only discussed the disordered state, but within the framework of the present theory we can also investigate the crystalline (face centered cubic) case. This case is simpler to treat analytically because only one kind of cells is involved (rhombic-dodecahedral cells). In this case the present theory reproduces the old free-volume theory or lattice theory [11, 15]. From elementary geometry, we can calculate the expressions for $v(\mathbf{n}^{\text{FCC}})$, $u(\mathbf{n}^{\text{FCC}})$, $\mathcal{P}(\mathbf{n}^{\text{FCC}})$ and from eq. (4) we can write $\ln Q$ as a function of ρ , which leads to $\frac{PV}{kNT} = (1 - (\frac{\sqrt{18}}{\pi}\rho)^{\frac{1}{3}})^{-1}$ (same as in [15]). As one can see from the graphical comparison given in fig. 1, this simple equation gives a prediction which is in good agreement with the results from numerical simulations.

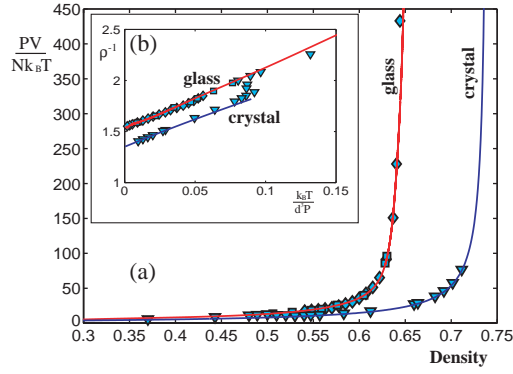


Fig. 1 – (a) Comparison between $\frac{PV}{Nk_B T}$ from numerical simulations for the ordered-FCC branch [19] (triangles), the disordered glassy branch [19] (squares), [23] (lozenges) and the predictions from the present theory (full lines). (b) The same data are plotted as ρ^{-1} vs. $k_B T/(d^3 P)$.

Let us now investigate the dynamical evolution of the system when the density increases up to the maximal packing. The quantity that measures the average mobility of the spheres between cells is $\langle \mathcal{P} \rangle = \sum_{\mathbf{n}} \frac{N^*(\mathbf{n})}{N} \mathcal{P}(\mathbf{n})$, which goes to 1 when all the local configurations are sufficiently closed packed such that the internal sphere cannot anymore escape from the “cage”

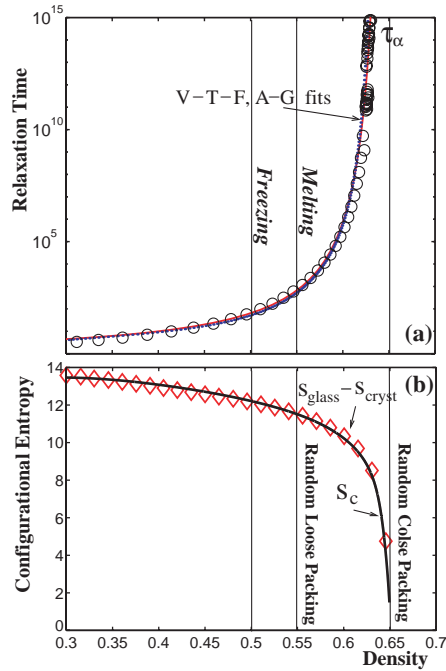


Fig. 2 – (a) Semi-log plots of the characteristic relaxation time τ_α vs. ρ . The lines are fits with Vogel-Tammann-Fulcher and Adam-Gibbs behaviors (full and dotted lines). (b) Configurational entropy vs. ρ (line) and the difference between the entropies of the disordered and crystalline phases (lozenges).

made by the external ones. The quantity $1 - \langle \mathcal{P} \rangle$ is therefore the probability to escape from such a cage and its inverse (τ_α) is proportional to the characteristic time of relaxation associated with the diffusion constant (the α -relaxation). When τ_α becomes infinitely large, the system is unable to fully explore the phase-space leading to a “quenching” into the disordered configuration. We observe (see fig. 2a) that the adimensional quantity $\tau_\alpha = (1 - \langle \mathcal{P} \rangle)^{-1}$ grows of more than an order of magnitude in the range of densities between $0.5 \leq \rho \leq 0.55$. (Note that these densities coincide with the metastable fluid-phase region [19,22,23] and the value $\rho \sim 0.55$ coincides both with the “melting point” and with the density of “loose disordered packings” found experimentally [31].) We verify that the behavior of τ_α vs. temperature is well described (when $\rho \geq 0.45$) with a Vogel-Tammann-Fulcher equation: $\tau_\alpha \sim A \exp[B/(\rho_{VF} - \rho)]$ (with $A = 0.6$, $B = 0.68$ and $\rho_{VF} \simeq 0.65$). This is the expected behavior in several glass-forming liquids [32,33] and it reproduces some experimental results for granular materials [8]. The same kind of behavior (with $B = 0.6$ and $\rho_{VF} = 0.64$) has been experimentally observed in the low shear viscosity of several colloidal systems [27]. Moreover, molecular dynamics of dense hard-spheres fluids with different polydispersities [34] yield to the same behavior with fitting parameters $B = 0.18$ and ρ_{VF} between 0.60 and 0.612 (depending on the polydispersity). The density $\rho_{VF} \simeq 0.65$ is very close to the empirical value for random close packing [9,18]. At this same density the configurational entropy ($s_c = -\sum_{\mathbf{n}} \frac{N^*(\mathbf{n})}{N} \log(\frac{N^*(\mathbf{n})}{N})$) goes to zero (fig. 2b). We have also verified that the Adam-Gibbs relation [2] $\tau_\alpha \sim A' \exp[B'/(Ts_c)]$ (with $A' = 2$ and $B' = 1.0\pi d^3 P/k_B$, fig. 2a) is well followed. Such relation has also been verified for a binary mixture of spheres using molecular dynamics [16]. Moreover, in fig. 2b it is also shown that the definition of s_c is consistent with the empirical definition of the configurational entropy as the difference between the entropies of the glass and crystalline phases.

In conclusion, we have presented a theory which combines some of the features of the free-volume and inherent-structures approach. Its application to hard-spheres system, in spite of some approximation involved, gives results in very good agreement with numerical simulation data [19,23,34] and some experimental data [27]. In this approach we have considered the space partition in single cells. To systematically improve the approximation, one should consider a larger group of cells as basic unit (supercell). The larger the supercell the better would be the approximation.

* * *

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