# Cell approach to glass transition

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**Abstract**
We present a novel theoretical approach to understanding the complex dynamics
of glass-forming liquids, granular packings and amorphous solids. This theory,
which is an elaboration of the free volume and inherent structure approaches,
allows one to retrieve the thermodynamical properties of these systems from
studies of geometrical and topological properties of local, static configurations
alone. When applied to hard-sphere systems, the present theory reproduces
with a good quantitative agreement the equation of state for the crystalline and
the disordered glassy phases. Moreover, we find that, as the density approaches
a critical value close to the random close-packing density, the configurational
entropy approaches zero and the large relaxation time diverges according to the
Vogel–Fulcher behaviour, following also the Adam–Gibbs relation.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Several natural and artificial systems, such as granular materials, glasses, cellular systems and
foams, present complex dynamical and structural properties despite the inner simplicity of their
fundamental elements [1]. In the context of glasses, there are many valuable theories based on
free volume [2], cooperative rearrangements of particles [3], the inherent structures approach
[4–6], mode coupling theory [7] and replica theory [8]. Here we develop a novel approach
(which combines some of the features of the free volume [2] and the inherent structures
approaches [4]) where we derive the structural and dynamical properties of large systems of
interacting particles from the local geometrical properties of space-filling sets of cells. This
approach 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 obtain insight into the intrinsic structures of solids, liquids and glasses,
to investigate biological tissues and to understand the bare nature of disorder [9–11]. For
this system, we retrieve quantitatively the equation of state for the glass and crystal phases.

We find that the relaxation time diverges as the density approaches the random close-packing limit [9, 12], following both the Vogel–Fulcher–Tammann law and the Adam–Gibbs relation.

## 2. Energy landscapes and inherent structures

A useful concept in glass theory based on the energy landscape was introduced by Goldstein in 1969 and later developed by Stillinger and Weber [4]. The energy landscape is associated with the potential energy $U(\{r_i\})$ as a function of the $3N$ particle coordinates. This energy landscape is characterized by deep minima. The idea is that in supercooled liquids at low temperatures, the particles vibrate around these deep minima, with some jumps from one minimum to another. In molecular dynamics simulations these minima, called 'inherent structures' [4], can be obtained by minimizing the energy starting from the liquid equilibrated at a given temperature [5]. If the minima are labelled by the index $\alpha$ and $F^\alpha$ is the free energy relative to the metastable state $\alpha$, the partition function $Q$ can be written as

$$Q = \sum_\alpha e^{-\beta F^\alpha} = \sum_F \Omega(F) e^{-\beta F}, \tag{1}$$

where $\Omega(F) = $ number of states corresponding to the free energy $F$ and is related to the configurational entropy $S_{conf}(F)$:

$$S_{conf}(F) = \ln \Omega(F) \tag{2}$$

with the equilibrium condition given by

$$\beta = \frac{\partial S_{conf}(F)}{\partial F}. \tag{3}$$

The configurational entropy has been evaluated for interacting particles by using both analytic [13] and molecular dynamics techniques [6, 13]. It was found that $S_{conf}$ at low temperature is a decreasing function of the temperature and can be extrapolated to zero at a temperature $T_K$, as expected by Kauzmann's argument.

## 3. The Adam–Gibbs approach

Adam and Gibbs have provided an interesting connection between kinetics and thermodynamics, by introducing the concept of cooperatively rearranging regions. According to this phenomenological theory, at low temperature, relaxation can only occur if an entire region of minimum size undergoes a cooperative rearrangement. Since this minimum size can be related to the inverse of the configurational entropy, it follows that the relaxation time $\tau$ can be expressed as

$$\tau \sim A \exp\left(\frac{B}{T s_c}\right), \tag{4}$$

where $s_c = S_{conf}/N$ is the configurational entropy per particle and $A$ and $B$ are constants. If $s_c$ goes linearly to zero at the Kauzmann temperature $T_K$, at the first order in $T - T_{VF}$, one recovers the Vogel–Tammann–Fulcher relation [14]:

$$\tau \sim A \exp\left(\frac{B'}{T - T_{VF}}\right), \tag{5}$$

with $T_{VF} = T_K$.

In this way the Adam–Gibbs theory predicts that if there is a thermodynamical transition where the configurational entropy goes to zero, then at this temperature the relaxation time—or the viscosity—diverges according to the Vogel–Tammann–Fulcher relation, as found in many glass formers.

## 4. Cell theory for dense liquids

We present here an approach introduced recently by us [15] to treat high-density liquids and to study the glass transition. This theory combines aspects of the free volume theory and the energy landscape approach. We consider first the free volume theory [17].

Let us first write down the configurational partition function of a system of $N$ particles:

$$Q(N, V, T) = \frac{Z}{N! \Lambda^{3N}}, \tag{6}$$

with $\Lambda = h/(2\pi mkT)^{1/2}$ and

$$Z = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \, e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)}, \tag{7}$$

where $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the potential energy. We observe that the integral over the whole volume can be written as a sum of integrals over a set of cells $C_{l_i}$:

$$\int_V d\mathbf{r}_i = \sum_{l_i=1}^{N} \int_{C_{l_i}} d\mathbf{r}_i. \tag{8}$$

Therefore, the configurational integral becomes

$$Z = \sum_{l_1=1}^{N} \cdots \sum_{l_N=1}^{N} \int_{C_{l_1}} d\mathbf{r}_1 \cdots \int_{C_{l_N}} d\mathbf{r}_N \, e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)}. \tag{9}$$

We now observe that these integrals can be written in terms of the occupation numbers $m_i$ (number of particles in each cell $C_i$, $0 \leqslant m_i \leqslant N$), leading to

$$Z = \sum_{m_1=0}^{N} \cdots \sum_{m_N=0}^{N} \frac{N!}{m_1! \cdots m_N!} Z(m_1, \ldots, m_N), \tag{10}$$

(with the constraint $\sum_i m_i = N$). Here, $Z(m_1, \ldots, m_N)$ is the contribution to the configurational integral of a system with $m_1$ spheres in the first cell, $m_2$ in the second etc:

$$Z(m_1, \ldots, m_N) = \overbrace{\int_{C_1} \cdots \int_{C_1}}^{m_1} \cdots \overbrace{\int_{C_N} \cdots \int_{C_N}}^{m_N} e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \, d\mathbf{r}_1 \cdots d\mathbf{r}_N. \tag{11}$$

The case where the cells are all singly occupied ($m_1 = m_2 = \cdots = m_N = 1$) contributes to $Z$ with

$$Z^{(1)} = Z(1, \ldots, 1) = \int_{C_1} \cdots \int_{C_N} e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \, d\mathbf{r}_1 \cdots d\mathbf{r}_N; \tag{12}$$

whereas the relative contribution with the cells multiply occupied is given by

$$\sigma^N = \sum_{m_1=0}^{N} \cdots \sum_{m_N=0}^{N} \frac{1}{m_1! \cdots m_N!} \frac{Z(m_1, \ldots, m_N)}{Z(1, \ldots, 1)} \tag{13}$$

(with $\sum_i m_i = N$).

From the previous definitions of $Z^{(1)}$ and $\sigma$, we can write

$$Z = N! Z^{(1)} \sigma^N. \tag{14}$$

If (as in the crystalline state at high densities with the cells constructed around the lattice positions) multiple occupancy of any cell is excluded, all of the $Z(m_1, \ldots, m_N)$ are zero except $Z^{(1)}$ and therefore

$$\sigma = 1. \tag{15}$$

In the opposite limit, when the particles are free to move among the cells,

$$\sigma^N \to \frac{N^N}{N!} \sim e^N. \tag{16}$$

This quantity $\sigma$ is called the 'communal entropy' and we have seen that it has the value $\sigma = 1$ for a crystal and $\sigma = e$ for a dilute gas, and it assumes some intermediate values in the liquid state.

## 5. Free volume and Hartree-like approximation

So far we have not made any approximations and equation (14) is an exact alternative way to *write* the configurational integral $Z$. However, to *calculate* these quantities, one must introduce some approximations. Let us now introduce a Hartree-like approximation by writing $Z^{(1)}$ as a product of quantities associated with each cell $C_i$:

$$Z^{(1)} = \int_{C_1} \cdots \int_{C_N} e^{-\beta U(r_1,\ldots,r_N)} \, dr_1 \cdots dr_N \simeq z_1 z_2 \cdots z_N; \tag{17}$$

it can be shown that [17]

$$-kT \ln Z^{(1)} \simeq \sum_{i=1}^{N} \left[ \epsilon_i - kT \ln \frac{u_i}{\Lambda^3} \right],$$

where $\epsilon_i$ is the average potential energy in the cell $C_i$ due to all other particles and $u_i$ is the 'free volume': the volume available in the cell $C_i$ with an appropriate weight depending on the interacting potential of the other particles [16, 17]. A similar approximation for $\sigma$ leads to

$$\sigma^N \simeq \prod_i \frac{1}{\mathcal{P}_i} \tag{18}$$

where $\mathcal{P}_i$ is the probability that cell $C_i$ is singly occupied.

In conclusion, the free energy can be written as

$$F \simeq \sum_i \left[ \epsilon_i - kT \left( \ln \frac{u_i}{\Lambda^3} - \ln \mathcal{P}_i \right) \right].$$

This approximate expression is based on the implicit assumption that the cellular partition is constructed around the equilibrium position of the particles [15, 17]. This holds good for a crystal, but not for a dense liquid or a glass where distinct configurations contribute with similar weights to the system free energy.

## 6. Cell theory for highly dense liquids and glasses

For a highly dense liquid we need a cellular partition which reflects the structure of the metastable states of the potential landscape. To this end, we write the configurational partition function as a sum over the metastable states labelled '$\alpha$'. These states are the points in the $3N$-dimensional configurational space $\{r_1^\alpha, \ldots, r_N^\alpha\}$ in which the probability of finding the particles is locally a maximum (inherent states [4]):

$$Q = \sum_\alpha e^{-\beta F^\alpha}. \tag{19}$$

For a given state $\alpha$, we divide the volume $V$ into $N$ cells $C_1^\alpha, \ldots, C_N^\alpha$ constructed around the positions $r_1^\alpha, \ldots, r_N^\alpha$. In this way we associate with each state $\alpha$ a space partition. Following the previous formalism, for each state $\alpha$ under the Hartree-type approximation we can write

$$F^\alpha \simeq \sum_i \epsilon(n_i^\alpha) - k_B T \left[ \ln \frac{u(n_i^\alpha)}{\Lambda^3} - \ln \mathcal{P}(n_i^\alpha) \right], \tag{20}$$

where the symbol $n_i^\alpha$ represents the set of parameters which carries the complete information about the geometrical and topological properties (size, shape, ...) of cell $C_i^\alpha$; $\epsilon(n_i^\alpha)$ is the energy contribution from a particle in the cell $C_i^\alpha$; $u(n_i^\alpha)$ is the *'free volume'* associated with the cell $C_i^\alpha$; and $\mathcal{P}(n_i^\alpha)$ is the probability of finding cell $i$ singly occupied. Note that the free energy depends only on the distribution $N^\alpha(n)$: the number of cells, in the space partition $\alpha$, characterized by the set of geometrical and topological parameters $n$ (therefore $F^\alpha = F(\{N^\alpha(n)\})$). It follows that the sum over the states $\alpha$ in equation (19) can be written as a sum over the space partitions $\{N^\alpha(n)\}$ associated with these states:

$$Q = \sum_\alpha e^{-\beta F(\{N^\alpha(n)\})} = \sum_{\{N(n)\}} \Omega(\{N(n)\}) e^{-\beta F(\{N(n)\})}, \tag{21}$$

where $\Omega(\{N(n)\})$ counts the number of distinct space partitions made with the set $\{N(n)\}$ and is related to the configurational entropy:

$$S_{conf} = \ln \Omega. \tag{22}$$

A rough approximation gives

$$\Omega(\{N(n)\}) \simeq \frac{N!}{\prod_n N(n)!} \tag{23}$$

which is an upper bound for $\Omega$, since some of these combinations do not generate space-filling assemblies.

The distribution $N^*(n)$ can be now evaluated by minimizing the free energy:

$$\frac{N^*(n)}{N} = \frac{u(n)}{\Lambda^3 \mathcal{P}(n)} \exp[-\beta\epsilon(n) - \theta v(n) - \lambda]. \tag{24}$$

Here, the two parameters $\lambda$ and $\theta$ are Lagrange multipliers which are fixed by the two constraints

$$\sum_n N^*(n) = N \tag{25}$$

and

$$\sum_n v(n) N^*(n) = V. \tag{26}$$

Using this distribution, the free energy is given by

$$\frac{\ln Z}{N} = -\beta \sum_n \frac{N^*(n)}{N} \left[ \epsilon(n) - kT \left( \ln \frac{u(n)}{\Lambda^3 \mathcal{P}(n)} - \ln \frac{N^*(n)}{N} \right) \right]. \tag{27}$$

## 7. Application to hard spheres

In these systems, the relevant parameter is the density $\rho$, which is 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 $\rho = \pi/\sqrt{18} = 0.7404\ldots$, which corresponds to the ordered arrangement found in face-centred cubic (FCC) crystals. This limit cannot be reached in disordered packings, where experimentally densities around 0.64 are found in the so-called *random close packing* [9, 10, 18].

There have been many studies on the nature of the hard-sphere glass transitions [19]. Experiments on colloidal systems seem to indicate a structural arrest close to a value $\rho = 0.57$ [20, 21]; this transition is characterized by a power law divergence for a large relaxation time and can be well described in terms of the mode coupling theory [22]. Molecular dynamics simulations have shown the presence of a glass transition around such values of
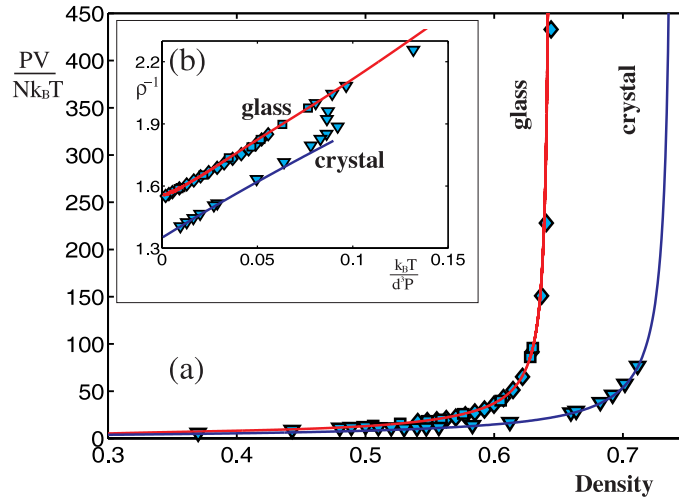
**Figure 1.** (a) Comparison among $\frac{PV}{Nk_BT}$ from molecular dynamics simulations for the ordered FCC branch ($\nabla$ [30]), the disordered glassy branch ($\square$ [30], $\Diamond$ [23]) and the predictions from the present theory (full curves). (b) The same data plotted as $\rho^{-1}$ versus $k_BT/(d^3P)$.

the density [23]. However, a more recent work excludes the possibility of such a transition [24]. Other experiments on colloidal systems [25–27] show that the approach towards the maximal disordered density is critical, with a viscosity that grows exponentially quickly (Vogel–Tammann–Fulcher behaviour) following the free volume prediction and the Adam–Gibbs relation. These results were also suggested on the basis of molecular dynamics data [28].

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 behaviour and satisfies the Adam–Gibbs relation.

## 8. Equation of state for the ordered crystal and the disordered glass

From the results presented in section 6 (equations (24) and (27)), it is clear that in order to calculate the distribution $N^*(n)$ and the free energy $\ln Z$, the only data required are the volumes $v(n)$, the free volumes $u(n)$ and the caging probability $\mathcal{P}(n)$ ($\epsilon(n) = 0$ for hard spheres) for a set of cells associated with attainable packings of spheres. In order to explore extensively the attainable local configurations, we generate more than $10^6$ compact local configurations with one central sphere and a number of neighbouring spheres in the range $5 \leqslant n \leqslant 16$ placed in a disordered fashion (but avoiding overlapping) at equal distance $h_0$ from the central one. Then we generate larger cells by uniformly expanding the compact ones from $h_0$ to $\sqrt{2}h_0$. The distance $h_0$ is a measure of the geometrical frustration [10, 15, 29] and it has been fixed at $h_0 = 1.058\,d$ (with $d$ the sphere diameter). We identify the cell $C_i^\alpha$ with the Voronoï cell (also known as the Wigner–Seitz cell or Dirichlet region) generated by bisecting with planes the segments between the centre of sphere $i$ and the centres of its neighbouring spheres. For each configuration we evaluate: (i) the volume $v(n_i)$ of the Voronoï cell; (ii) the free volume $u(n_i)$; (iii) the caging probability $\mathcal{P}(n_i)$.

Once we have obtained these quantities, we derive the distribution of cells from equation (24) and therefore the free energy from equation (27), from which we obtain the

equation of state:

$$P = k_B T \left( \frac{\partial \ln Z}{\partial V} \right)_{N,T}. \tag{28}$$

The comparison with data obtained from molecular dynamics simulations for hard spheres [23, 30, 31] is shown in figure 1.

Within the framework of the present theory we can also investigate the crystalline case. This case is simpler to treat analytically because only identical rhombic-dodecahedral cells are involved. We have

$$\frac{PV}{kNT} = \left[ 1 - \left( \frac{\sqrt{18}}{\pi} \rho \right)^{1/3} \right]^{-1}. \tag{29}$$

The comparison with the molecular dynamics simulation data is also shown in figure 1.

## 9. Relaxation time and the Adam–Gibbs relation

Using the distribution $N^*(n)$ we calculate the escape probability

$$\langle \mathcal{P}_{esc} \rangle = \sum_n \frac{N^*(n)}{N} \mathcal{P}_{esc}(n), \tag{30}$$

where $P_{esc}(n) = 1$ or $0$ depending on whether the configuration of the cell $n$ is such that the external spheres allow or do not allow the sphere inside the cell to escape.

We observe that the relaxation time $\tau = \langle \mathcal{P}_{esc} \rangle^{-1}$ grows by more than an order of magnitude in the range of densities $0.5 \leqslant \rho \leqslant 0.55$ and its behaviour versus density is well described by a Vogel–Tammann–Fulcher equation:

$$\tau \sim A \exp(B/(\rho_{VF} - \rho)) \tag{31}$$

with $\rho_{VF} = \rho_K \simeq 0.65$ (figure 2(a)).

We have also calculated the configurational entropy per particle $s_c$:

$$s_c = -\sum_n \frac{N^*(n)}{N} \log\left( \frac{N^*(n)}{N} \right), \tag{32}$$

which goes to zero at the Kauzmann density $\rho_K \simeq \rho_{VF} \simeq 0.65$ (figure 2(b)). Moreover, we verify that the definition of $s_c$ is consistent with the definition of the configurational entropy as the difference between the entropies of the glass and crystalline phases (figure 2(b)).

We finally observe that the Adam–Gibbs relation

$$\tau \sim A' \exp(B'/(T s_c)) \tag{33}$$

is followed (figure 2(a)).

## 10. Conclusions

In conclusion, we have presented a theory which combines some of the features of the free volume and inherent structures approaches. Its application to hard-sphere systems, despite the approximations involved, reproduces many of the known properties of these systems. In particular, the results for the equation of state are in very good agreement with molecular dynamics data. Moreover, the theory reproduces well the Vogel–Fulcher–Tammann law, the Adam–Gibbs relations and the behaviour of the configurational entropy. This is also in agreement with recent experiments on colloidal systems.
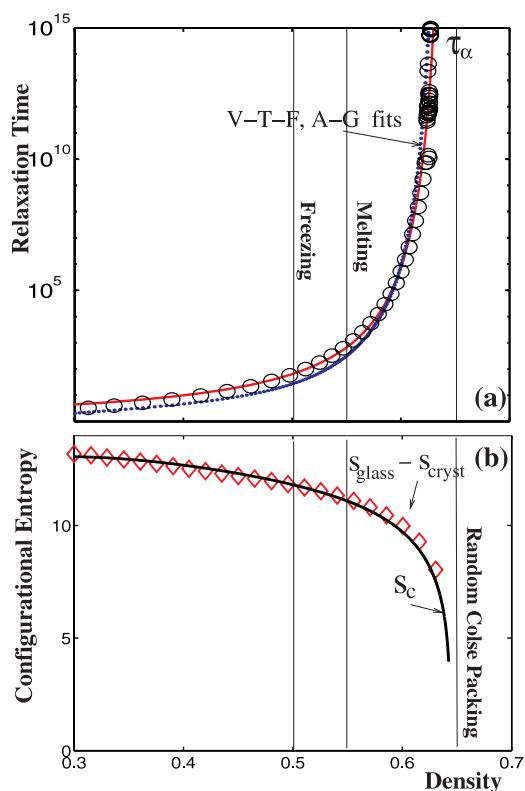
**Figure 2.** (a) Semi-log plots of the characteristic relaxation time $\tau_\alpha$ versus $\rho$. The curves are fits with Vogel–Tammann–Fulcher and Adam–Gibbs behaviours (full and dotted curves). (b) Configurational entropy versus $\rho$ (curve) and the difference between the entropies of the disordered and crystalline phases ($\Diamond$).

We stress that a strong approximation in this work is the identification of the number of possible configurations with the combinatorial factor $N!/\prod_n N(n)$. This approximation ignores the condition of space filling. To take the space-filling condition into account better, one should go beyond the single-cell approximation and consider a larger group of cells as the basic unit: a *supercell* (under the condition that the cells inside the supercell must satisfy the space-filling condition). The larger the supercell, the better the approximation.

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