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On the occasion of the 70th birthday of Constantino Tsallis

# Cell Theory of the Glass Transition

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LI CORSO - VARENNA SUL LAGO DI COMO - VILLA MONASTERO - 27 Luglio - 8 Agosto 1970

# Glassy Materials

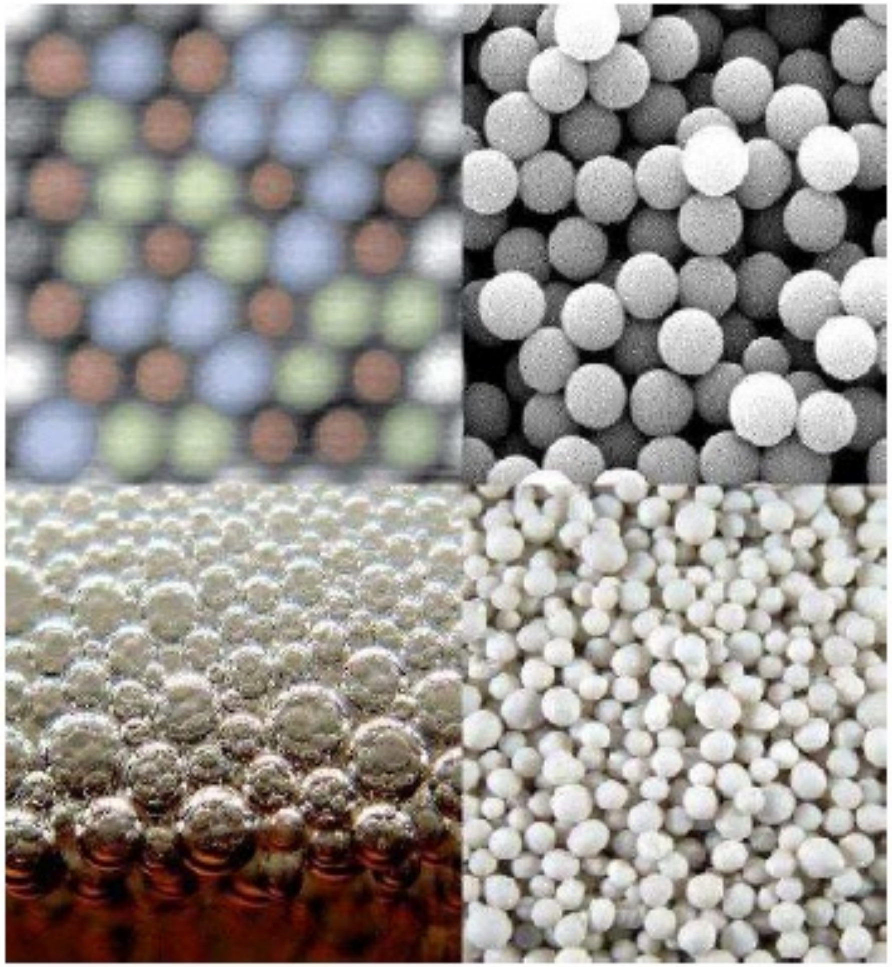
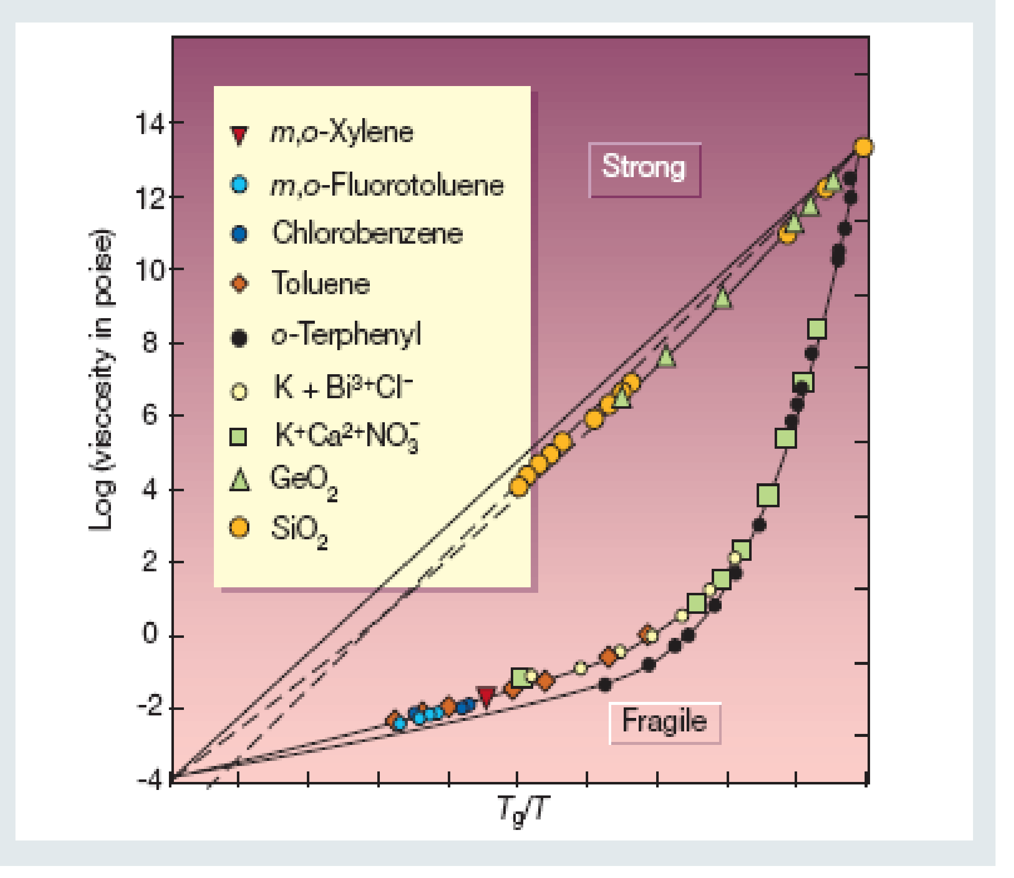


FIG. 1 Glassy phases occur at low temperature or large density in many different systems spanning a broad range of lengthscales, such as atomic (top left), colloidal (top right) systems, but also in foams (bottom left) and granular materials (bottom right). **Berthier & Biroli 2010**

# Glass Transition

ANGELL
PLOT




**Debenedetti and Stillinger Nature 2001**

$$\tau,\eta = A\exp\left[\frac{E}{T}\right]$$

**Arrhenius**

**(Strong)**

$$\tau,\eta = A\exp\left[\frac{B}{T-T_0}\right]$$

**VFT**

**(Fragile)**

# MODE COUPLING THEORY

Gotze and Sjogren
Rep Prog Phys 1992
Gotze J. Phys Cond Matt 1999

Gotze and collaborators derived from first-principles an equation for the time dependent density autocorrelation function , which makes a number of precise dynamical prediction.

$$\tau \approx A(T - T_C)^{-\gamma}$$

This behaviour however is not what is found experimentally, Tc nowdays is believed to represent only a crossover towards an exponential type of behavior with a divergence at much lower temperature.

# MORE THEORIES OF THE GLASS TRANSITION

Free Volume Theory  mostly developed by Cohen and Turnbul

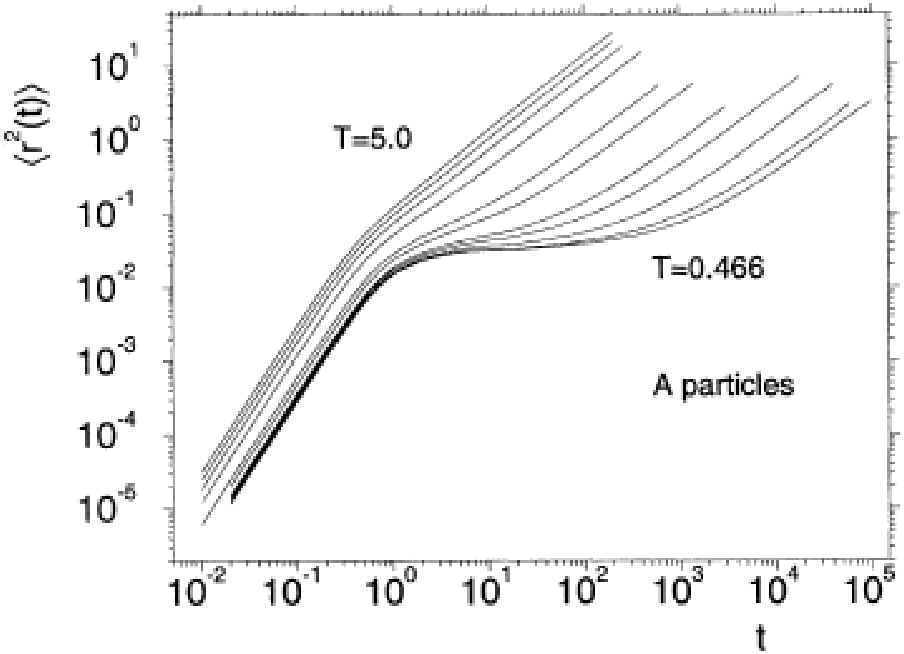
Cooperative Rearranging Region originally proposed by Adam and Gibbs and now incorporated in its modern version of the Random First Order Transition (RFOT) introduced by Kirkpatrick, Thirumalai and Wolynes, who played, among many others, an important role in its development.

Each theory captures some correct  aspect  of the glass transition. It is then  plausible that the “final” theory must reproduce the essential features of  these different approaches.

In this talk, after briefly reviewing FV theory and CRR theory I will present the Cell Theory of the Glass Transition, which we have recently proposed. I will show that this approach reproduces in  fact the essential ingredients of both  Free Volume and Cooperative Rearranging Regions in a unified manner leading to new predictions.

# Cage Effect Glassy Systems

**Mean square displacement**



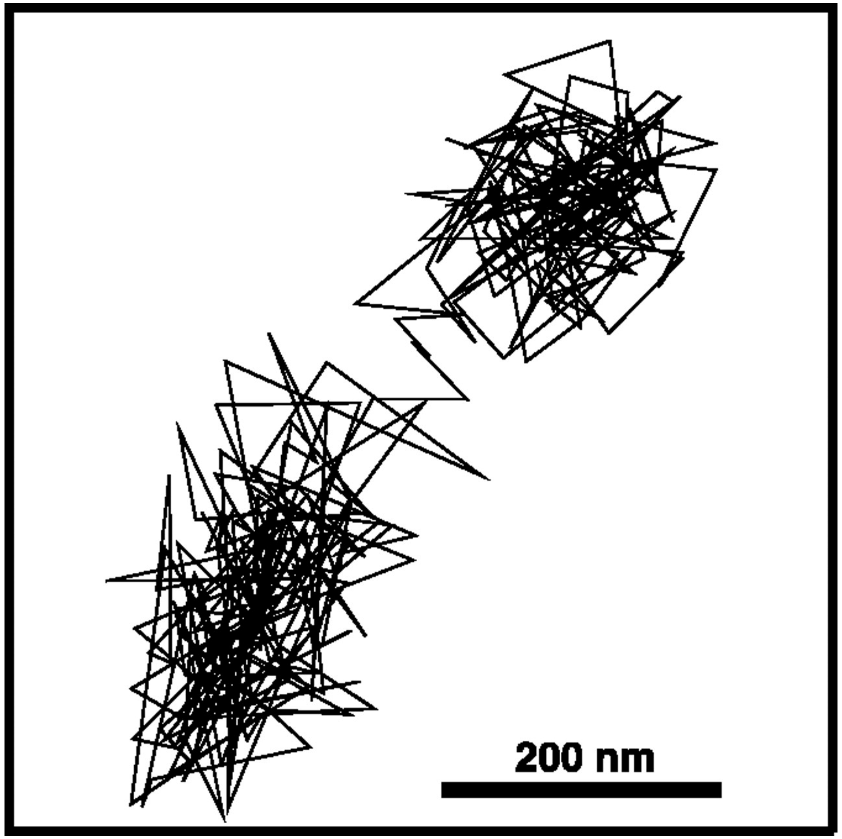

**Lennard -Jones mixture MD simulations**

**Kob and Andersen PRL 1994**

**CAGE EFFECT**

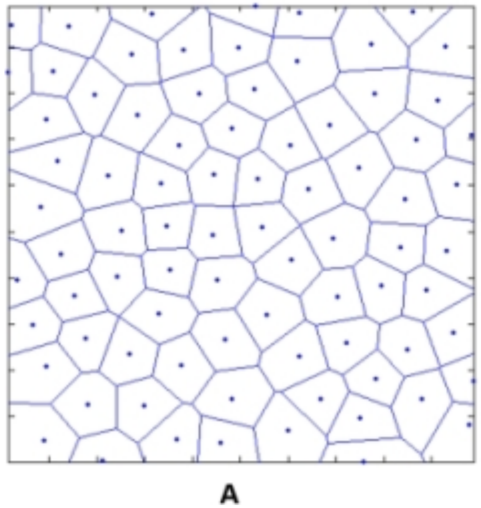
Weeks, Crocker, Lewitt,Schofield,
Weitz, Science 2000

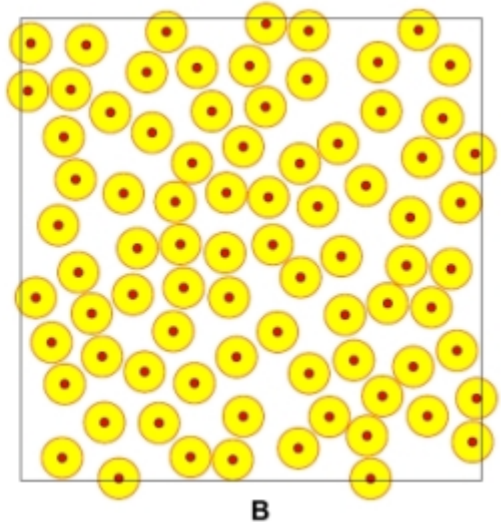
Evidence of cage effect in colloidal suspension




A typical trajectory for volume fraction 0.56

# FREE VOLUME THEORY




VORONOI TESSELLATION HARD SPHERES

Consider for simplicity a colloidal system which can be described as a system of hard sphere particles.The system can be divided into N cells, constructed around the particle positions.

Each particle can move in a free volume v, where the center of a sphere can translate, given that all other particles are fixed.

Roughly we can say that the particle rattles in a cage of its free volume.

# FREE VOLUME PROBABILITY DISTRIBUTION

Cohen & Turnbull 1959

**Say $N_i$ the number of particles with free volume $v_i$ supposed to be descretised**

$$\sum_i N_i \mathrm{v}_i = V_f \quad \text{total free volume} \qquad \sum_i N_i = N \quad \text{total number of particles}$$

$$W\{N_i\} = \frac{N!}{\prod_i N_i!}$$

Number of ways of redistributing the free volume

$$\text{Maximize } W\{N_i\} \qquad N_i = A\exp(-\beta \mathrm{v}_i)$$

**finally passing to the continuum limit one gets the distribution p(v)**

$$p(\mathrm{v}) = \frac{1}{<\mathrm{v}>}\exp(-\mathrm{v}/<\mathrm{v}>)$$

**p(v)dv probability to find a particle in a free volume between v and v+dv**

**$<v> = V_f/N$**

# RELAXATION TIME IN THE FREE VOLUME THEORY

**If a particle is in a cage with small volume fraction v the probabbility to excape will be small. In a simple approach it is assumed that, below a threshold v<v*, the particle is localised, otherwise it jumps and gets out of the cage.**

**The probability P that a given particle jumps out of the cage is given by the probability that the particle has a free volume v >v*:**

$$P = \int_{\mathrm{v}^*}^{\infty} p(\mathrm{v}) d\mathrm{v} = \exp(-\mathrm{v}^* / < \mathrm{v} >)$$

**And the relaxation time (the time to get out of the cage)**

$$\boxed{\tau = 1/P = \exp(\mathrm{v}^* / < \mathrm{v} >)}$$

# Free Volume Theory
# Relaxation time as function of temperature T

**Within the free volume theory Cohen and Turnbull estimates that the average free volume goes to zero linearly with the temperature**

$$< \mathrm{v} >= T - T_0$$

$$\boxed{\tau = \exp A/(T - T_0)}$$

**The relaxation time diverges following the Voghel-Fulcher-Tamman law in quite good agreement with the experimental data.**

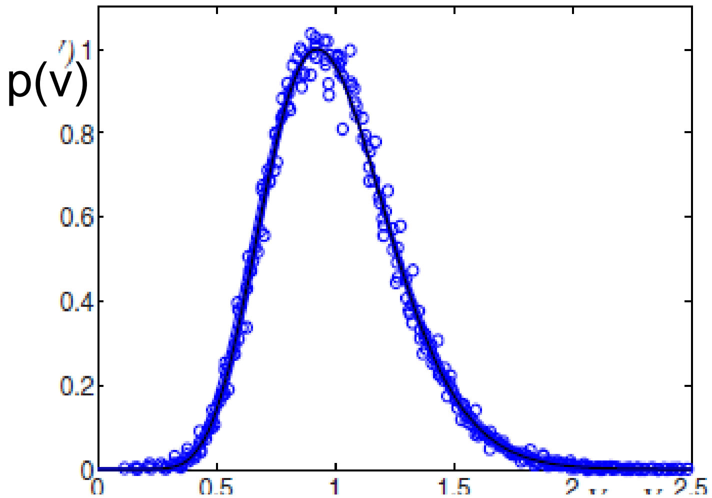
# Failure of the F V T for the free volume distribution

**Free volume theory predicts  a pure exponential**

$$p(\mathrm{v}) = \frac{1}{<\mathrm{v}>} \exp(-\mathrm{v}/<\mathrm{v}>)$$

**Numerical simulations on hard spheres and experimantal data on granular materials show a fit with a Gamma distribution**

**Aste, Di Matteo PRE 2008**




**Gamma distrinution for different volume fraction btween 0.55 and 0.64, values of k between 12 and 14**

**See also Ciamarra,Nicodemi, Coniglio PRE 2007 (simulations  granular packings).**
**Starr, Sastri, Douglas, Glotzer PRL 2002 (simulations of polymer melt, water and silica)**

$$p(\mathrm{v}) = \frac{k^k \mathrm{v}^{k-1}}{\Gamma(k) <\mathrm{v}>^k} \exp(-k\mathrm{v}/<\mathrm{v}>)$$

**Where k si a fitting parameter**

## COOPERATIVELY REARRANGING REGIONS

Adam and Gibbs (1958)
Kirkpatrick Thirumalai Wolynes (1989)

An alternative theory was introduced by Adam and Gibbs (1958), who introduced the concept of cooperatively rearranging regions.

The main idea is that close to the glass transition due to the crowding of the particles, the decay towards equilibrium of a density fluctuation is due to a cooperative rearrangement of an entire region.

A cooperative rearranging region of linear size $\xi$. can be defined as the smallest region that can be rearranged without involving particles outside its boundary.

It is argued that the relaxation time diverges exponentially with $\xi$

$$\tau = A \exp D\xi^{d} = A \exp \frac{B}{T - T_0}$$

.

# CELL THEORY OF THE GLASS TRANSITION

Aste, A.C. 2002,2003,2013

**We start from first principls and apply a statistical mechanics formulation which was introduced to study high dense fluid (Hill: Statistical Mechanics 1965) The partition function of a system of N undistinguishable particles in a volume V at a temperature T is given by:**

$$Z = \frac{1}{N!\Lambda^{dN}} \int_V dr_1 \dots \int_V dr_N e^{-\beta U(r_1,\dots,r_n)}$$

$$\Lambda = (h^2 / 2\pi m k_B T)^{1/2}$$ **thermal wavelevgth**

**Divide the entire volume in cells . The cells are built around the particles positions .**
**The integral over the volume can be decomposed in the sum over the integral of a single cell.**

$$\int_V dr_i = \sum_{l_i=1}^{N} \int_{C_{l_i}} dr_i$$

**Under the hypothesis of high density, it is possible to show that the partition function is given by:**

**Aste, Coniglio 2002,2003,2013**

$$Z = \sum_{\{N_i\}} \Omega(\{N_i\} e^{-\beta f(\{N_i\})}$$

$$-\beta f(\{N_i\}) = \sum_i N_i [\ln \frac{v_i}{\Lambda^d}]$$

**i is an index which characterizes the cell and $N_i$ is the number of cells of type i, while $v_i$ is the free volume associated to the cell i.**

**$f(\{N_i\})$ is the free energy for a fixed distribution $\{N_i\}$**

$$\Omega(\{N_i\})$$

**Number of distinct configurations characterised by the same distribution $\{N_i\}$**

According to the free volume theory $\Omega(\{N_i\})$ Is given by

$$W(\{N_i\}) = \frac{N!}{\prod_i N_i!}$$

However this represents an upper limit, as some of these combinations of cells do not generate space fillings assemblies. In fact according to the picture of the cooperative rearranging regions, we can argue that only a fraction of cells

$N/\lambda$ with $\lambda = \rho\,\xi^d$ $\rho$ particle density

can be considered in this exchange, since most of the cells within the cooperative rearranging regions are in a jammed state and do not partecipate to the rearrangement. Therefore

$$\Omega(\{N_i\}) = \frac{(N/\lambda)!}{\prod_i (N_i/\lambda)!}$$

**Insert into the expression of the partition function and minimize the free energy with respect to the distribution $\{N_i\}$, one gets the equilibrium distribution $\{N_i^*\}$. Finally passing to the continuum limit:**

$$p(\mathrm{v}) = \frac{k^k \mathrm{v}^{k-1}}{\Gamma(k) < \mathrm{v} >^k} \exp(-k\mathrm{v} / < \mathrm{v} >)$$

**p(v)dv probability to find a particle in a cell with free volume between v and v+dv**

**$k = k_0 + \lambda$ with $k_0$ = constant and $\lambda = \rho \xi^d$**

**In agreement with the Gamma distribution found in experiments and numerical results. Here k assumes a particular meaning related to the cooperative length**

# RELAXATION TIME

$$\tau^{-1} \approx P = \int_{v^*}^{\infty} p(\mathrm{v})d\mathrm{v}$$

v* is the free volume of a cell below which the particle cannot excape.

The integral is a incomplete Gamma function and can be evaluated.
We find two regimes

1) An apparent power law regime for low density, or low temperature <v> >v*

$$\boxed{\tau = A(<\mathrm{v}> - \mathrm{v}_c)^{-1}} \qquad \mathrm{v}_c \cong \mathrm{v}^*$$

**2) An exponential regime for high density or high temeperature <v> < v***

$$\tau = B\exp(a\frac{v^*}{<v>} + \lambda\frac{v^*}{<v>})$$

**With B and a constant and** $\lambda = \rho\xi^d = b\frac{v^*}{<v>}$

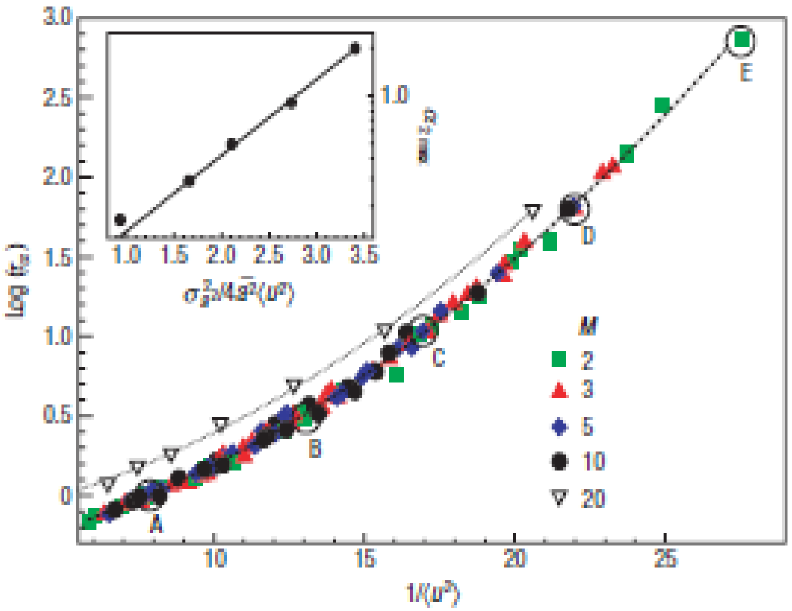
$$\tau = A\exp\left(\frac{c}{<v>} + \frac{d}{<v>^2}\right)$$

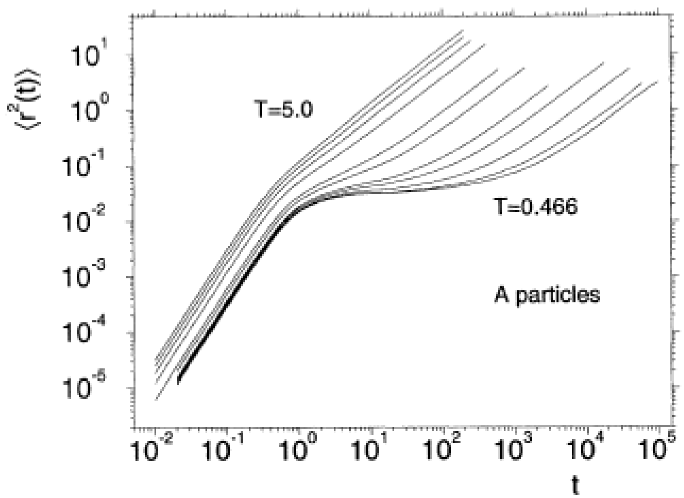
**Note that the first part reproduce the free volune , while the second part is dominated by the cooperative lenght**

This expression has to be compared with a similar expression proposed by Larini et al to fit a huge mass of experimental and numerical data

$$\tau = A\exp\left(\frac{\beta}{<u^2>} + \frac{\gamma}{<u^2>^2}\right)$$

**Larini, Ottochian, De Michele, Leporini Nat Phys 2008**




Where $<u^2>$ is the mean square diplacement corresponding to the plateau, and therefore is related to the size of the cage

To know the behaviour as function of the temperature, we have to express <v> as function of the temperature.

If we use the expression suggested by the free volume theory :

$$< \mathrm{v} >= D(T - T_0)$$

$$\tau = A \exp\left( \frac{c'}{T - T_0} + \frac{d'}{(T - T_0)^2} \right)$$

# Connection with non extensivity entropy

$$\Omega(\{N_i\}) = \frac{(N/\lambda)!}{\prod_i (N_i/\lambda)!} = \left[\frac{(N)!}{\prod_i (N_i)!}\right]^{1/\lambda}$$

$\lambda = \rho\xi^d \quad \lambda \to N^x \quad \mathrm{x} \leq 1$ at the glass transition

$$\ln\Omega = \frac{1}{\lambda}\ln\left[\frac{(N)!}{\prod_i (N_i)!}\right] = \frac{N}{\lambda}\,\mathrm{s}_{\mathrm{FV}}$$

Far from the glass transition

$$\ln\Omega \approx N \quad \text{extensive}$$

At the glass transition

$$\ln\Omega \approx N^y \qquad \mathrm{y} = 1\text{-x} \leq 1 \qquad \text{non extensive}$$

# CONCLUSIONS

**We have proposed a statistical mechanical approach to the glass transition which contains features of**

**Mode Coupling**
**Free Volume**
**Cooperative Rearranging Regions**

**It predicts :**

**Gamma distribution for the free volume in agreement with numerical and experimental data.**

**A relaxation time with an apparent power law divergence (Mode Coupling).**

**A crossover towards an exponential behavior first dominated by the free volume distribution then followed by a stronger divergence dominated by a cooperative Length.**

Happy Birthday Constantino

and many more

years of creative and

fruitful research