Glass transition
And out-of-equilibrium systems

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Contents

Chapter 1

An introduction to glassy systems

Despite intense research the glass transition resists a deep microscopic understanding. As a consequence there is no widely accepted explanation of the glass transition. However glass transition, understood as a brutal (exponential) arrest of relaxation of some degrees of freedom, has been observed in a large number of systems : super-cooled liquids (the common glasses), colloids, granular matter,spin glasses, optimization problems...This empirical fact rises the question of the universality of glass transition. As we shall see, this question has recently led to the emergence of a new concept perhaps more general and in any case easier to define, the concept of dynamical heterogeneity.

In this brief chapter, we will first introduce the gross phenomenology [3, 19, 9], which is the obliged starting point. We give, in the second section, what is in our mind the physical setting of the glass transition by analyzing the relation between time and length scales. This leads to the introduction of dynamical heterogeneities in a third section. The last section is devoted to the main scenarii depicting glass transition. For all this chapter we send the interested readers back to the recent review of L.Berthier and G.Biroli [4].

1.1 Phenomenology

We present here three examples of glassy systems : super-cooled liquids, colloids and driven granular systems. We will see that although these three systems are all experimenting some kind of dynamical heterogeneity, the physical meaning and the related models may be quite different.

1.1.1 Molecular glass formers

These systems are usually described by a pairwise potential. The standard Hamiltonian being given by :

$$H_{MGF} = \sum_{i<j} V(|\overrightarrow{r_i} - \overrightarrow{r_j}|) \ , \tag{1.1}$$

where the potential could be generally decomposed in two parts : a repulsive core part and and attractive part, the most popular one being the Lennard-Jones potential. We just add that as long as we are interested in standard glass transition, the dynamics is simply given by a classical Newtonian one.

The most salient fact in observing molecular glass former is the dramatical increase of the relaxation times with the temperature : a decrease of a third of the melting temperature leads to an increase of fourteen orders of magnitude in relaxation times. This increase is seen both in experiments, where pressure is in general kept constant, and numerically, where the volume does not vary. One can see for example in the figure (1.1) the effect of this increase on some thermodynamic observable like specific volume. The liquid is cooled down fast enough to avoid crystal nucleation and fall out-of-equilibrium at an empirical temperature which depends of the cooling rate. This behavior has been observed for a vast majority of liquids, the so-called super-cooled liquids.

For practical purpose an experimental glass temperature T_g is defined as the temperature corresponding to a viscosity of 10^{12} Pa.s. Measurement of viscosity have shown a surprising behavior : some liquids follows an Arrhenius law, others do not (see figure (1.2)). The first are called strong liquids, the other fragile liquids. The *fragility* of a liquid is then defined as the deviation from the Arrhenius law. This concept will play a important role in the following interpretations of glass transition. Let us just mention here that this fragility is commonly thought as an effect of some kind of collective behavior.

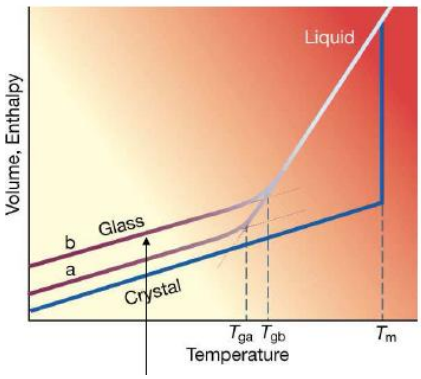

Figure 1.1: Glass transition : some thermodynamics

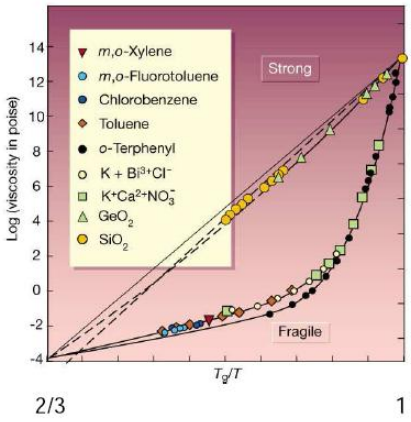

Figure 1.2: Relaxation times of glass formers : strong and fragile liquids. Temperatures are rescaled by the glass transition temperature T_g

1.1.2 Colloidal glasses

With colloids we change of length scale. Colloids are big particle, with a typical radius of 1 to 500 nm, dipping in a thermalized liquid. The motion of colloids is just a reflect of thermal fluctuations in the solvent. The most naive description of colloids is given by a hard sphere interaction potential which is a fair approximation as long as the colloids do not interact via electrostatic or magnetic,... potentials. This is a first difference with supercooled liquids.

The second one is the dynamics. In the case of colloids the dynamics is to good extent described by the Brownian motion :

$$\partial_t \overrightarrow{X_i} = -\partial_{\overrightarrow{X_i}} H + \eta_i(t) \tag{1.2}$$

$$< \eta_i(t)\eta_j(t') > = D_{eff}\delta_{ij}\delta(t-t') \tag{1.3}$$

Finer descriptions could be used taking into account subtle hydrodynamics effects (memory kernels,...). We shall say that the temperature only gives the microscopic timescale on which a particle diffuse.

The tuning parameter is here the density and more precisely the volume fraction $\Phi = \frac{4\pi}{3}R^3\rho$. A dynamical arrest or *jamming transition* is observed (see figure (1.3)), with a 6 to 7 order increase in time scales. An interesting feature of this system is that if one tunes the polydispersity of particles, namely their size distribution, one could avoid the crystallization.

1.1.3 Driven granular matter

We reach macroscopic length scale with driven granular matter. We are now interested in 2 or 3 dimensional grains (R$\simeq$1 mm). As a consequence of their size, those systems are a-thermal. That's why a driving force cannot be avoided, one has to deal with a non-equilibrium stationary state (NESS). Different forcings are used : shear, tapping, oscillating shears... A precise model is quite uneasy to define because of the insertion of friction. Anyway a dynamical arrest could be observed with an increase in relaxation times of 6 orders of magnitude.

Despite of their NESSie nature, driven granular systems could display the same phases as colloids (crystal in 3d, hexactic order in 2d,...)

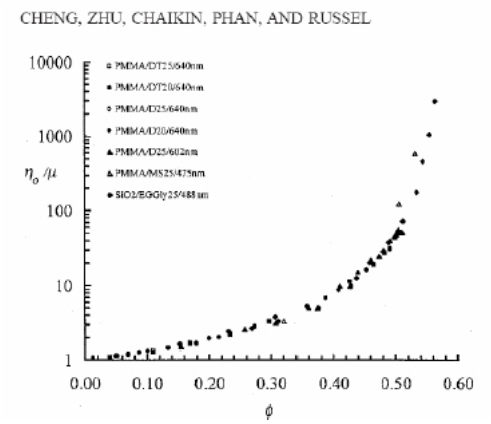

Figure 1.3: Viscosity of a colloid as a function of the volume fraction.

1.2 What is glassiness ?

What have all this systems in common ?

- *A strong increase of the relaxation times*, in particular for super cooled liquids. Moreover, similar fitting functions are used, the most popular one being the Vogel-Fulcher law :

$$\tau_{VF} \propto e^{D\frac{T_0}{T-T_0}} \tag{1.4}$$

  where D is the so-called fragility.

- *Qualitative features in the microscopic dynamics.* If one is interested in some correlation function (e.g. density-density correlations for a super-cooled liquid, mean-square displacement for grains,...see next section for a precise definition), one observes a short-time decorrelation and the appearance of a plateau and finally a long-time relaxation. This usually interpreted as the fast thermalization of the particle in the cage formed by its neighbors (see figure (1.4)) and by its "jump" outside of this cage at longer times which leads to the complete relaxation in the very long time regime (see figure (1.5) and (1.6)) This is known as the

cage effect. In a more sophisticated language, the interpretation is that some degrees of freedom are frozen, leading to an average amorphous profile with valleys. The short-time dynamics is then related to some vibrations around the minima, the jump from a minima to an other being related to the plateau existence. This scheme is reminiscent of spin glasses.

- *No obvious diverging length scale accompanying the time increase* contrary to standard critical phenomena. Despite a huge amount of experimental and numerical works, no static increasing length has been found.

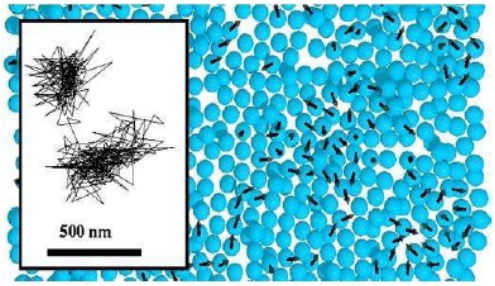

Figure 1.4: Cage effect in the real space. In the inset is plotted a typical trajectory of a particle.

More on the super-cooled liquids thermodynamics.

Based on the idea of a rough landscape and of amorphous minima, the concept of *configurational entropy* has been introduced. The idea is to count the number of amorphous minima :

$$S_c = \ln \mathcal{N}_{amorphous\ states} \tag{1.5}$$

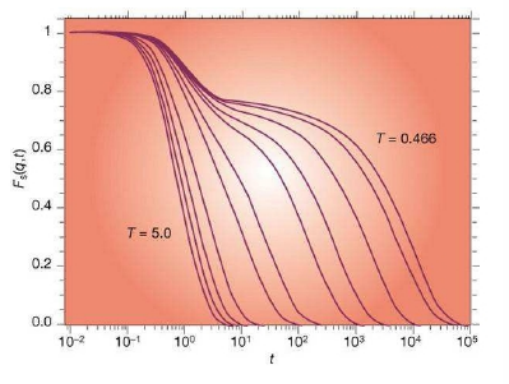

Figure 1.5: Evolution of the Fourier transform of the density-density correlator for a super-cooled liquid : appearance of a plateau, cage effect

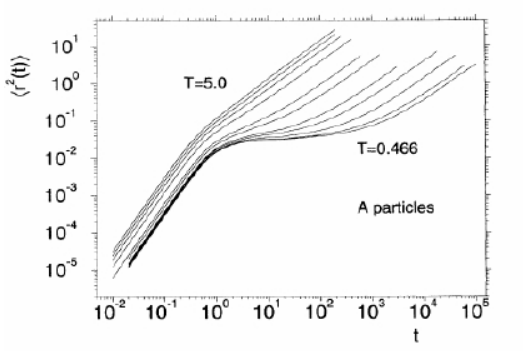

Figure 1.6: Evolution of the mean-square displacement : appearance of a plateau, cage effect

A proxy for the configurational entropy is conjectured to be the *excess entropy* defined as :

$$S_{exc} = S - S_{crystal} \tag{1.6}$$

One does the (unverified) assumption that the vibrations around the amorphous minima are similar to the ones for crystalline states. One can observe on figure (1.7) that an extrapolation of this measurements leads to a vanishing of the excess entropy at some finite temperature defined as the *Kauzmann temperature* T_K. This cancellation is also known as Kauzmann paradox. The paradox seems to be that the disordered state could have a lower entropy than the ordered one. There is here no paradox : this is indeed the case for hard spheres. In that case we are led to maximize entropy. If the spheres are identical the stable phase is a crystal (this is no longer true with some polydispersity). So that $S_{crystal} > S_{dis}$.

However, this extrapolation shows a striking fact : the extrapolated T_K is remarkably close to of the T_0 extrapolated from Vogel-Fulcher like fits of the relaxation time for a huge number of molecular glass formers (see table 1.8)

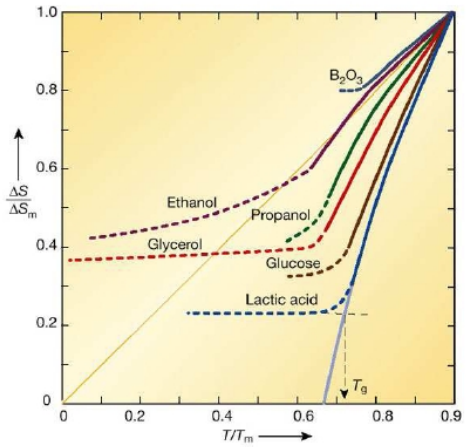

Figure 1.7: Extrapolation of the configuration entropy.

Substance	o-terphenyl	Salol	2-methyltetra-hydrofuran	n-propanol	3-bromopentane
T_K[K]	204.2	175.2	69.3	72.2	82.5
S_∞ [J K^{-1} mol^{-1}]	137.4	138.4	97.5	70.9	99.0
A	−13.73	−15.9	−17.3	−10.53	−12.9
B [K]	684.0	823.5	406.6	385.6	374.1
T_0 [K]	202.4	(175.2)	69.6	70.2	82.9
ΔT [K]	246–268	220–265	91–107	97–125	107–298
T_x [K]	246	220	91	97	108
$\kappa = B_{lo}/B_{hi}$	9.6	5.56	3.25	1.18	≈ 1
T_g [K]	290	265	107	138	(137)
T_{fin}[K]	331	315.0	138.8	148.8	167.3
T_{fin}/T_K	1.623	1.798	2.003	2.061	2.028
T_K/T_0	1.009	(1)	0.996	1.028	0.995
T_g/T_K	1.42	1.51	1.54	(1.73)	(1.66)

Figure 1.8: Comparison of the Vogel-Fulcher temperature with the Kauzmann temperature.

1.3 Dynamical heterogeneities

The existence of a diverging times scale at finite temperature (T≠0) is, in a general statistical mechanics setting, believed to be the result of an underlying growing length scale. A heuristic argument is the following : in a short-range system, one can divide the space into independent pieces of size ξ, the largest correlation length in the system. Relaxation times scale are necessarily lower than the time needed to rearrange all the particles of the cluster (or a finite fraction of it), that is $\tau \leq e^{K\xi^d}$. This inequality implies that if τ diverges there should be a diverging ξ.

Basic tools

Some experiments have shown that space time fluctuations increase approaching T_g, some simulations have lead to the same conclusion.The idea has been proposed that there is a diverging (or at least growing) length accompanying the slowing down of the dynamics. This is not a static but a dynamic length. The quantitative probe to measure this length is :

$$G_4(\overrightarrow{r},t) = < C(0,t)C(\overrightarrow{r},t) >_c \tag{1.7}$$

where, for example,

$$C(\overrightarrow{r},t) = \delta\rho(\overrightarrow{r},0)\delta\rho(\overrightarrow{r},t) \tag{1.8}$$

Here the analogy with the critical phenomena is total if we think $C(\overrightarrow{r},t)$ as some kind of dynamical order parameter.

We can associate to G_4 a susceptibility χ_4 defined as :

$$\chi_4 = N < \left(\frac{1}{V}\int d\overrightarrow{r}\,\delta C(\overrightarrow{r},t)\right)^2 > \tag{1.9}$$

$$= \rho \int d\overrightarrow{r}\, G_4(\overrightarrow{r},t) \tag{1.10}$$

the second relation standing at equilibrium (translation invariance).

As numerical accessible times are limited to something like six decades (thua much less than experimental timescales), we need of experimental accessible quantities. Let us define the global correlation function and the density of

enthalpy :

$$F(t) = \frac{1}{V}\int d\overrightarrow{r}\ \delta C(\overrightarrow{r},t) \tag{1.11}$$

$$h(t) = \frac{1}{N}(E+PV) \tag{1.12}$$

In the NPT ensemble, assuming equilibrium, a Cauchy-Schwarz inequality gives

$$\chi_4 \equiv N < F(t)^2 > \ \geq N\frac{< F(t)h(0) >_c^2}{< h(0)^2 >_c} \tag{1.13}$$

Fact is that each term of the left side of the inequality is experimentally accessible. Indeed, using the fact that in an equilibrated system :

$$N < h^2 >_c = T^2 C_p \tag{1.14}$$

$$\frac{d}{dT} < F(t) > = \frac{N}{T^2} < F(t)h(0) >_c \tag{1.15}$$

we obtain :

$$\chi_4 \geq \frac{T^2}{C_p}\left(\frac{d}{dT} < F >\right)^2 \tag{1.16}$$

Length and time scales

From the definition of χ_4 we can extract a length : if for example $G_4 \propto e^{-\frac{r}{\xi}}$, $\chi_4 \propto \xi^d$. For the sake of clarity, we assume as it is usual in critical phenomena a scaling form for F(t)= $f(\frac{t}{\tau})$, referred as time-temperature superposition in glass literature. As a result :

$$\chi_4 \geq \frac{T^2}{C_p} f'(1)^2 \left(\frac{d}{dT}\ln\tau\right)^2 \tag{1.17}$$

We see that if τ increases with decreasing temperature, so does χ_4. But, the most exciting point is this bound is that a good estimate of χ_4, since they have the same singular behavior. For an experimental use of this bound, see figures (1.9) and (1.10)

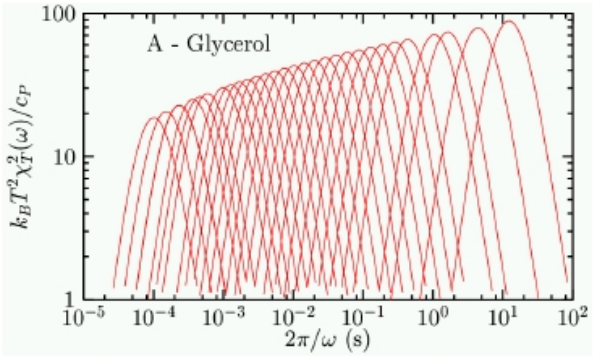

Figure 1.9: Experimental measurement of the bound (1.17) extract from the dielectric susceptibility of the glycerol [5]

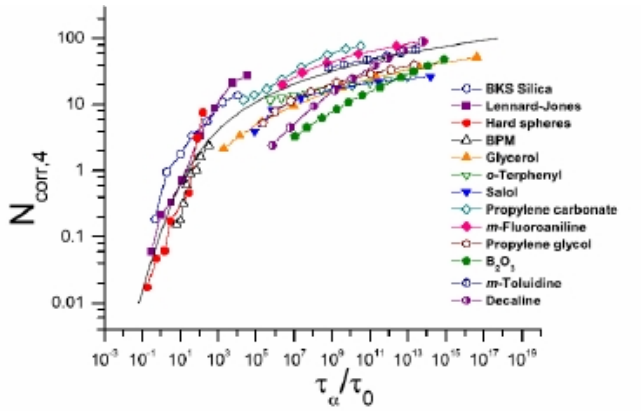

Figure 1.10: Experimental estimate of the number of correlated particles from the bound (1.17) on various glass formers. Due to an indeterminate normalization, this number could be lower than one on this plot.

1.4 Questions and remarks

What are the different scenarii extracted from the phenomenology ? Do they depend on the considered systems ?

- One possibility is that we face a new kind of thermodynamic transition, but with very strange features.
- A second one is that the glass transition is a pure dynamical transition (if it exists). What about grains ? Colloids ?
- A third possibility is that there is just a cross-over, an avoided transition. Super-cooled liquids ?

Chapter 2

Kinetically constrained models

Kinetically constrained models, or *KCM's*, are a very popular example of stochastic models on lattice. They are rather simple and have greatly contributed to recent progresses on glass transition by giving solvable examples and by reshaping the debate on glass transition nature. If the first proposed models (like Kob Andersen model) were only based on kinetic constrains (*i.e.* the microscopic realization of cage effect) with a trivial thermodynamics, recently introduced models have added the ideas of cooperativity and of phase transition to KCM zoology.

In the first section, we will give some general features of stochastic lattice models. In a second section we will introduce the original non-cooperative KCM's and in a third section their cooperative counterparts in infinite dimension. The fourth section will be devoted to the entropic barriers arising in finite dimensional cooperative models. The last section we will present a the spiral model, that is a KCM with a true dynamical transition.

2.1 A few words on stochastic models

Stochastic models are a drastic simplification of real particles problem. In this setting, particles instead of moving in the continuous space with a Newtonian dynamics, are constrained to evolve on a lattice with a dynamics determined by transition rates. Such simplification found its basis on the idea

of universality : if there is some diverging, or at least increasing, cooperative length, microscopic details of the lattice are washed out and we tend to the continuous limit.

More over the stochastic dynamics is not arbitrary. If we write the evolution of the probability of a configuration :

$$\partial_t P(\mathfrak{C}, t) = \sum_{\mathfrak{C}'} W(\mathfrak{C}' \to \mathfrak{C}) P(\mathfrak{C}', t) - \sum_{\mathfrak{C}'} W(\mathfrak{C} \to \mathfrak{C}') P(\mathfrak{C}, t) \tag{2.1}$$

We impose that the transition rates should verify a detailed balance condition in order to regain equilibrium properties (Gibbs measure) :

$$W(\mathfrak{C}' \to \mathfrak{C}) \frac{e^{-\beta E(\mathfrak{C}')}}{Z} = W(\mathfrak{C} \to \mathfrak{C}') \frac{e^{-\beta E(\mathfrak{C})}}{Z} \tag{2.2}$$

It is easy to check that the Gibbs measure is invariant (*i.e.* it does not evolve under the dynamics), and if one adds an irreducibility condition, that is the transition rates are such defined that any configuration could be reached after some steps from any initial configuration, Gibbs measure is the unique invariant measure (for finite number of site).

A stronger theorem exists [6]. It states that for a short-range system satisfying the condition of irreducibility, in the thermodynamics limit,

- For $d = 1$ and $d = 2$, the Gibbs measures are the only invariant probability measures.
- For $d \geq 3$, the translationally invariant Gibbs measures are the only translationally invariant probability measures.

But it is believed that $d = 1$ and $d = 2$ results are in fact valid for higher dimensions. A dynamical transition, where many invariant measure appear, has to be accompanied by a thermodynamic transition characterized by many Gibbsian measures. This suggests that a pure dynamical transition does not exist because KCM's have a trivial thermodynamics. However KCM's may exhibit a pure dynamical transition because they do not satisfy the irreductibility hypothesis. The argument stands in a drawing (see figure(2.1)) : the two disks can not explore all the space, there is unaccessible configurations. Fortunately simple rules on dynamics could be find to break irreducibility.

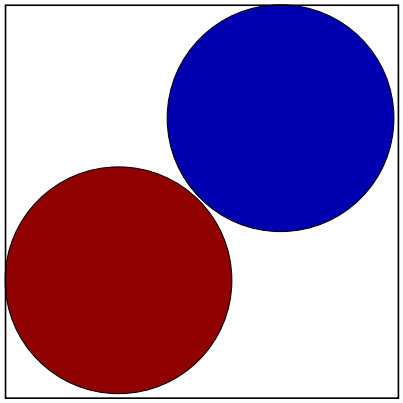

Figure 2.1: Irreducibility break down : all the space can not be visited

2.2 Non-cooperative models

2.2.1 Kob-Andersen model

The Kob-Andersen model [16] is a model of particles on a lattice. The number of particles is fixed. The kinetic constrain is chosen to mimic cage effect. For example, on a square lattice, a particle is mobile if the number of occupied neighbors is lower than 3 before and after the jump.

The Gibbs measure is flat. In the grand canonical ensemble, the partition function could be calculated, displaying no phase transition:

$$\begin{aligned} \Xi &= \sum_{\mathfrak{C}} \frac{1}{N!} e^{-\mu N} && (2.3) \\ &= \sum_{n_i=0,1} e^{-\mu \sum_i n_i} && (2.4) \\ &= (1+e^{-\mu})^N && (2.5) \end{aligned}$$

We also see that the density :

$$\rho \equiv \frac{N}{V} = \frac{e^{-\mu}}{1+e^{-\mu}} \qquad (2.6)$$

2.2.2 Fredrickson-Andersen model

This model is based on the concept of facilitated dynamics. Consider a coarse-grained portion of liquid, a bit more than a particle diameter. One would say this square is mobile if particles inside move for more than a particle diameter. The basic concept is that in order to relax at a given site one needs mobile neighbors.

The Fredrickson-Andersen model [14] is defined as a collection of N independent Ising spins in a field h. A spin is mobile if it is down. The dynamical rules are, for example on a square lattice, that an up spin flips with probability one and a down with probability $e^{-\beta h}$. The dynamical constraint to be verified to flip is that the number of up neighbors is lower than 3.

Again the thermodynamics is trivial, one can show for example that the concentration of up spins and the entropy per spin are given by :

$$c = \frac{1}{1+e^{\beta h}} \tag{2.7}$$

$$s = \ln(2\cosh\beta h) - \beta h \tanh\beta h \tag{2.8}$$

2.2.3 KCM as defects model

The Kob-Andersen model in the high density limit, as well Fredrickson-Andersen model in the low temperature limit, can be seen as independent defect models. For example, Kob-Andersen model on a square lattice with the constraint that the number of occupied neighbors is lower than 4 is nothing else than the standard lattice gas. The same model on a triangular lattice with the constraint that the number of occupied neighbors is lower than 5 has an interesting feature : an isolated blank can not move but two close enough blanks leads to a defect which is mobile.. One can show that the density of defects in the dense limit is proportional to $(1-\rho)^2$ with a diffusion coefficient for the defect of order one.As defect models, this models are good candidate to describe strong liquids, which have an Arrhenian relaxation time.

Defects models emerge also for kinetically constrained spin models. Let us take the example of the Fredrickson-Andersen model at $d = 1$ with the constrain that the number of down neighbors are more than 1 and $h = 1$. Consider a down spin in the middle of up spins. The probability that a up neighbor of the down spin flips is equal to $e^{-\beta}$. The probability that one

the two down spins flips is one. The result is : a down spin moves of one step on a time $\tau \propto e^{\beta}$. So the diffusion coefficient of defects is of order $e^{-\beta}$.

We can compute χ_4 in this case of non-interacting defects (d=3). Let us define the persistence $\Pi_x(t) =< P_x(t) >$, where $P_x(t)$ is equal to one if the spin at site x has not flipped between 0 and t, zero otherwise. In other words, $\Pi_x(t)$ is the probability that no defect has reached site x between 0 and t, this is also the mean over all the initial conditions of the probability that a defect at a site i does not reach x between time 0 and t. Using this last definition and the fact that the probability to reach site x coming from a site y is only a function of $|y-x|$, we see :

$$\Pi_x(t) = \frac{1}{V}\left[\sum_{y,y\neq x} P_{y-\times\rightarrow x}(t)\right]^{N_d} \tag{2.9}$$

$$= \frac{1}{V}\left[\sum_{y,y\neq x} 1 - P_{y\rightarrow x}(t)\right]^{N_d} \tag{2.10}$$

$$= \exp(-\rho_d - \rho_d \sum_{y,y\neq x} P_{y\rightarrow x}(t)) \tag{2.11}$$

where ρ_d is the density of defects. $\sum_{y,y\neq x} P_{y\rightarrow x}(t) = \sum_{x,x\neq y} P_{y\rightarrow x}(t)$, by translation invariance, is nothing else that the number of sites visited by the random walk, it is proportional to cD_dt. Introducing $\tau_{relax} = \frac{1}{\rho_d D_d}$, in d=2 :

$$\Pi_x(t) = \exp\left(-\rho_d - \frac{t}{\tau_{relax}}\right) \tag{2.12}$$

This relaxation time could be understood as follow (in d=2) : each defect visits D_dt sites in a time t, the defects being independent they visit $N\rho_d D_d t$ sites in a time t. The system has relaxed when all sites have been visited by at least one defect. Equaling $N\rho$ and $N\rho_d D_d t$ leads to $\tau_{relax} \simeq \frac{1}{\rho_d D_d}$. With the same line of thoughts, G_4 and χ_4 can be evaluated :

$$G_4(\overrightarrow{r},t) = \frac{c_r}{\rho_d} e^{-2\frac{t}{\tau_{relax}}} \left(\frac{t}{\tau_{relax}}\right)^2 f(\frac{\overrightarrow{r}}{\sqrt{D_d t}}) \tag{2.13}$$

where,

$$f(x) = \frac{1}{(2\pi)^{3/2}} \int_0^1 du \int_0^u d^3x \; e^{-\frac{x^2}{2}} \tag{2.14}$$

$$\chi_4(\overrightarrow{r},t) = \frac{c_r}{\rho_d}\left(\frac{t}{\tau_{relax}}\right)^2 e^{-2\frac{t}{\tau_{relax}}} \tag{2.15}$$

This last result shows that $\chi_4 \propto \rho_d(D_d t)^2 = \frac{1}{\rho_d}\left(\frac{t}{\tau_{relax}}\right)^2$. That means, reminding that $D_d t$ is the number of sites visited by one defect, the fluctuations of the persistence contributing to χ_4 are those visited by the same defect. We see an example of a dynamical correlation without any trace of cooperativity as the defects are independent.

2.3 Cooperative models

Three facts signal the presence of some cooperativity. Consider for example the Kob-Andersen model in two dimensions with the constraint that the number of occupied neighbors should be lower than 2. The first is the observation that a finite set of vacancies can not move in a completely filled lattice. Moreover, this is the second fact, if there is some blocked structure it must be infinite (see figure (2.2)). The last observation is that in these models an ergodicity breaking is necessarily associated with to a *jamming percolation*.

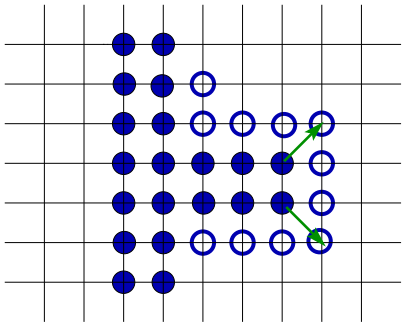

Figure 2.2: Necessity of infinite cluster of blocked particles.

Jamming percolation

We start with a "mean-fieldish" approximation of the problem. We consider the jamming percolation on random graphs, this will allow us to construct

recurrence equations that are easily solvable [25]. The jamming percolation, if present, will be given by the fixed point of the recursions.

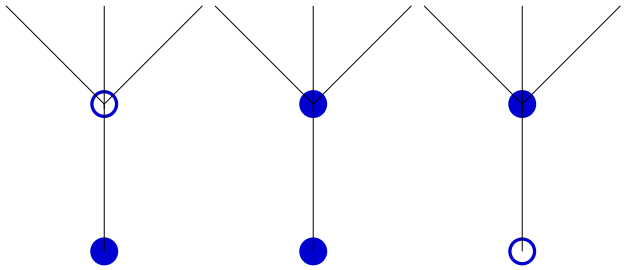

Figure 2.3: Element of recursion for the Kob-Andersen model in two dimensions with the constraint that the number of occupied neighbors should be lower than 2 (from left to right events referred as B, F and Y). B : a blank cannot be filled even though there is a particle downward. F : a particle cannot move forward if there is a particle downward. Y : a particle cannot move forward if there is a particle downward.

Let us introduce $\mathcal{G}_C$ the set of graphs having at each edge a connectivity equal to C. It is well known that the elements of $\mathcal{G}_C$ are tree-like in the sense that loops have a typical length of order lnN, and can be neglected. For the square lattice, we are interested in $\mathcal{G}_4$. For the sake of clarity, we take again the Kob-Andersen model in two dimensions with the constraint that the number of occupied neighbors should be lower than 2, there is 2^3 possibilities to block a particle. But, to construct the recursions, we only need the three events described in the figure 2.3. As an exercise, we invite the reader to reconstruct the recursions :

$$Y' = \rho\left[Y^3 + 3Y^2(1-Y) + 3B^2Y + B^3\right] \quad (2.16)$$
$$B' = (1-\rho)F^3 \quad (2.17)$$
$$F' = \rho\left[B+Y\right]^3 \quad (2.18)$$

Introducing $G = Y + B$ to obtain only one self-consistent equation, fixed point equation become :

$$F = \rho G^3 \quad (2.19)$$
$$B = (1-\rho)\rho^3 G^9 \quad (2.20)$$
$$G = 3\rho G^2 - 2\rho G^3 + (1-\rho)\rho^3 G^9 - 6(1-\rho)\rho^4(G^{10} - G^{11}) \quad (2.21)$$
$$+ \; 3(1-\rho)^2\rho^7(G^{18} - G^{19}) \quad (2.22)$$

Analyzing the solutions of the last equation, one finds : i) there exists a transition at a given and finite $(G_c, \rho_c) \simeq (0.758, 0.888)$, ii) the transition is discontinuous. Moreover, rewriting equation (2.22) $G = \mathcal{F}[G, \rho]$ one notes, and expanding around the right side of the transition :

1. $\frac{\delta}{\delta G}\mathcal{F}[G_c, \rho_c] = 1$

2. $\delta G \propto \sqrt{|\rho - \rho_c|}$

This cluster which contains a finite fraction of the particles is also fragile. If one removes one particle, one sees that $\frac{1}{\sqrt{\delta\rho}}$ particles are released. This fragility is associated with a correlation length diverging like $\delta\rho^{-\frac{1}{2}}$. Numerical results argue for a relaxation time and a dynamical susceptibility (χ_4) diverging with *power laws*, this result differs significantly from Vogel-Fulcher-like divergence. It is now widely accepted that this power laws are able to explain the first six decades of relaxation time, this regime is called MCT (see the next chapter). One explanation could be a hidden Ginzburg criterion : far enough from the critical point the system is "mean-field". Then appears a cross-over to a Vogel-Fulcher regime.

2.4 Entropic barriers

As we have shown in the previous section, the transition is discontinuous. For the standard first-order transitions, it is well known that in finite dimension nucleation occurs, with an activated barrier given by surface tension. There is here some similarities except from the essential fact that the barrier to overcome has an entropic origin. More precisely we will show that there exists a given system size above which it is possible to nucleate macro-defects causing the relaxation of the system, *i.e.* restoring ergodicity.

We have said that KCM's may display a dynamical transition but no thermodynamic phase transition [26]. A fact is : in the thermodynamics limit the part of the phase space which is not irreducible tends to be of null measure. The proof goes in two times, we show that : i) we first identify the set of the configurations where each particle can be moved, this is the set of frameable configurations, ii) we show that this set contains almost all the configurations (with probability one) in the limit N$\rightarrow \infty$.

Irreducibility of frameable configurations

We call *framed configuration* (see figure (2.4)) a configuration which only have blanks on its surface, a *frameable configuration* a configuration which could be framed after a certain number of allowed moves.

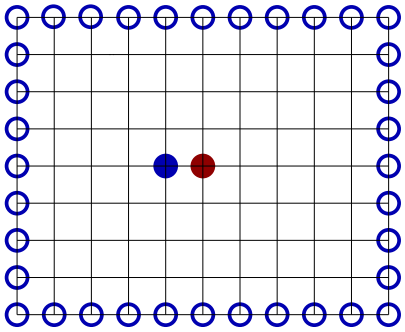

Figure 2.4: A frameable configuration for a particle model at $d = 2$

To be specific, consider the Kob-Andersen model in two dimensions with the constraint that the number of occupied neighbors should be lower than 2 on the square lattice (others are similar but more complicated). One can show that any particle could be swapped with its neighbors after some allowed moves if the configuration is framed. The demonstration stands on the drawings of the figure (2.5). We only use the fact that to be displaced a blank just needs another blank as a neighbor. The recurrence is initiated at the edge and propagate until it is possible to invert the red particle (or blank) and the blue one. Thus, frameable configurations are irreducible since it is possible to swap any particles by leaving all the others in their initial position.

Entropic barriers and frameable configurations

Let us consider a square of size L. Assuming there is a framed configuration of size $l < L$, how does this defect increase ? It just needs to have two blanks neighboring each side of the framed square to grow from l to (l+2) (see figure (2.6)).

Now we can compute the probability to have a framed configuration generated by this recursion. The probability $p_2(l)$ of having two blanks near a

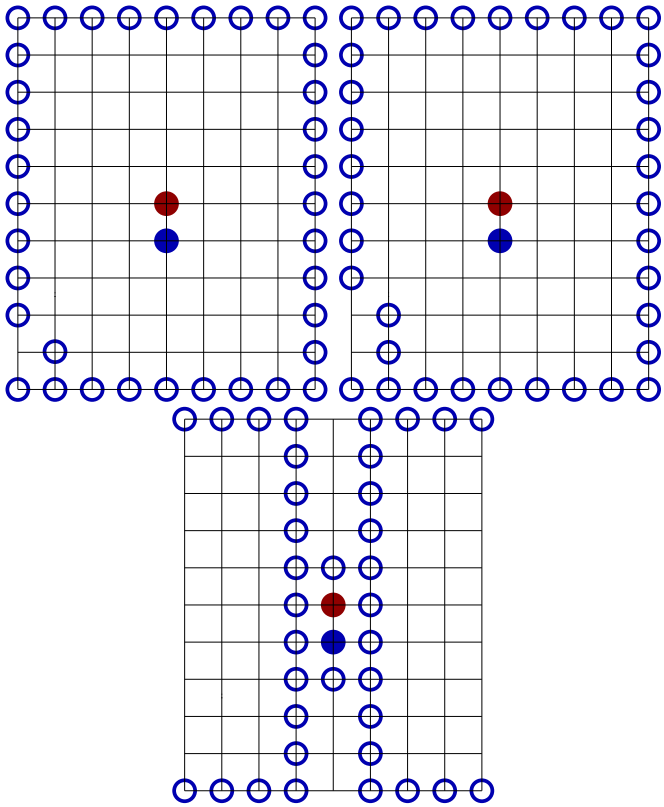

Figure 2.5: Irreducibility of frameable configurations.

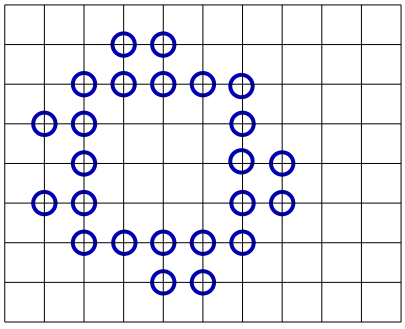

Figure 2.6: From l-framed square to (l+2)-framed square.

line of length l is given by :

$$p_2(l) = 1 - \rho^l - l(1-\rho)^{l-1} \tag{2.23}$$

And the probability to find a framed configuration is starting from x :

$$P_f(x) = (1-\rho)^4 \prod_{n=1}^{L/2} (p_2(2n))^4 \tag{2.24}$$

It could be shown that in the limit $1 - \rho \to 0$:

$$(1-\rho)P_f(x) = -cste \tag{2.25}$$

Since we can start from many different seeds, the typical length where frameable configurations appear is given by $L^2 P_f(x) = \mathcal{O}(1)$[1]. So the critical length verifies surely the following inequality :

$$\ln(L_c) < \frac{cst}{2(1-\rho)} \tag{2.26}$$

It can be also shown that if L is two small, there is some blocked structure. Reasoning on this doubled lined infinite structure, one obtains :

$$\ln(L_c) > \frac{cst'}{2(1-\rho)} \tag{2.27}$$

By adjusting the two constants of the upper and lower bounds, one obtains equality for : $cste = \frac{\pi^2}{9}$.

One can identify frameable configurations and a seed with macro-defects. From equation (2.25) in the limit $\rho \to 1$, we see the typical size of framed squares, defined as the size above which one can continue the infinite iterative process with probability close to one, is $-\frac{\ln(1-\rho)}{1-\rho}$ and the typical distance between them by $e^{\frac{cste}{1-\rho}}$. They can move using the vacancies on their boundaries. Studies have shown they diffuse with a diffusion constant $D \propto \exp(\frac{c}{\sqrt{1-\rho}})$.The relaxation time is just given by :

$$\tau = \simeq \frac{1}{\rho_d D_d} \simeq e^{\frac{cste}{1-\rho}} \tag{2.28}$$

We have to wait that macro-defects (framed squares) diffuse across the system.

[1]The rigorous proof is a bit more subtle but the key idea is here.

In three dimension, for a number of occupied neighbors less or equal to three, one could show with the same kind of reasoning that :

$$\tau = \exp\exp(\frac{cste}{1-\rho}) \tag{2.29}$$

2.5 Spiral model, d=2 glass transition

This model [24], or SM, is an example of KCM displaying a true dynamical transition. This is a two dimension spin model where a spin can be flipped if the two spins of two adjacent plaquettes are simultanously down (see the figure (2.7) for the notation. The flipping rate is p for going from down to up, and 1-p otherwise. This model shares interesting features with directed bond percolation (DBP).

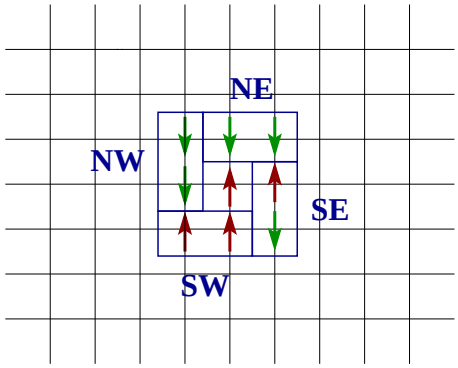

Figure 2.7: Definition of spiral model(SM).

Indeed, if we draw two arrows pointing to the spins of the NE plaquette, we obtain a lattice strictly identical to the one of DBP. Follow a cluster of up spins developing in the NE/SW axes. Focus on a spin inside. One notes that this site because of the kinetic constraints is blocked. Thus, the presence of a DBP spanning cluster leads to a blocked spin chain. We obtain the bound : $p_c \leq p_c^{DBP}$.

In fact, we can prove the equality. But before doing, let us note a slight difference between BDP paths and SM's ones. A NW/SE of finite extension could be blocked by intersecting NE/SW path and so does not need to be infinite to be stable (this is a T-junction, see 2.8). This observation

completely change the property of the transition. The main result is that the relaxation times have essential singularities forms and no more power law shapes.

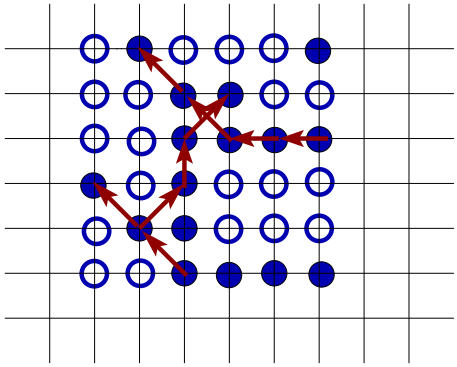

Figure 2.8: An example of T-junction.

The proof is similar to the one for bootstrap percolation. It starts with an empty square centered in x (drawn on the tilted lattice previously introduced) of size $\sqrt{2}l$ with two spins at each edges. There is four sites which needs to be empty to propagate the empty structure from as size l to (l+1) as indicated on figure (2.9). Taking the green site to the left on the figure (2.9), one sees a l-NESW-path is needed to block this site in a up (occupied) configuration. As $\rho < \rho_c^{BDP}$ there is a probability $\exp(-\frac{cl}{\xi_{/\!/}})$ to have a path of size l ($l >> \xi_{/\!/}$) at this green point, where $\xi_{/\!/}$ is the correlation length of the DBP along the axis. The cost for a one-step expansion of the empty structure has a cost : $1 - 4\exp(\frac{cl}{\xi_{/\!/}})$. Since the correlations among events at different l's are positive, the probability of the emptying procedure is bounded by below by the product of the one-step expansion probabilities. :

$$P_{empty,x} \geq (1-\rho)^{c^2\xi_{/\!/}^2} \prod_{l=c\xi_{/\!/}}^{\infty} 1 - 4\exp(-\frac{cl}{\xi_{/\!/}}) \tag{2.30}$$

As $\rho < \rho_c^{BDP}$, $\xi_{/\!/} < \infty$: $P_{empty,x}$ has a finite positive value. This completes the proof : the emptying procedure has a finite probability to happen. As there is a finite fraction of sites from which all the lattice could be emptied, $p_c \geq p_c^{DBP}$. This gives the equality.

We give without any justifications, the interested reader is referred to the literature [24], the property of the SM transition :

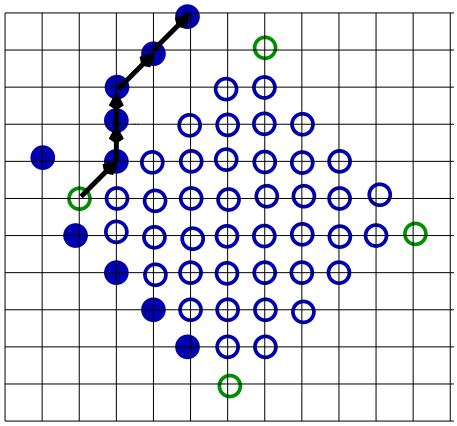

Figure 2.9: Propagation/blockade of empty (down) structure

1. This transition is discontinuous : the number of blocked sites jump from a null value to a finite number across the transition.

2. The cross-over length, *i.e.* the typical size below which frozen clusters occur on finite lattice, is exponential : $lnL_c = cst|p - p_c^{BDP}|^{-\mu}$, where μ is given by the exponents of the BDP.

3. The relaxation time has also an essential singularity characterized by the same exponent : $ln\tau = cst'|p - p_c^{BDP}|^{-\mu}$

A few words of conclusion. This KCM's reproduce an important part of the phenomenology of glassy systems : there is no static diverging length, the transition when it occurs is discontinuous, the time divergence shows the good behaviors, a dynamical length scale appears clearly. Nevertheless, it is quite unclear how to choose the good rules. Shall we consider models displaying a transition like the spiral model, or not like in the Kob-Andersen model ? Why shall we take a particular kinetic constraint rather than an other ? Clearly, in the future, one shall study the universality of these models and their kinetic rules. In particular, one would like to know the universality of the spiral model transition, its property in three dimension....

The super-cooled liquids seem not to be well described by this models, they are likely better models for colloids and granular matter. The two main difficulties are : i) they cannot explain why T_K and T_0 are so close, ii) $\xi_4 \simeq L_c$ does not grow so fast, but like $\ln \tau \propto \xi_4$. An alternative point of

view is surely needed.

Chapter 3

RFOT and rough energy landscapes

Based on a rough free energy landscape picture, the random first order theory (RFOT) [21, 22] is a scenario to describe fragile molecular glass formers. If the very idea of cooperative rearranging regions is traced back to the work of Adam and Gibbs, it has only acquired a microscopic basis with the emergence of the spin glass theory. The main present result is a clear "mean-fieldish" formulation of the glass transition for fragile liquids, the most salient result being the exact identity of the dynamics of some generalized spin-glass models (like the p-spin model) with those of the mode coupling theory (MCT), a standard theory of liquids. Using this analogy, a scenario for the finite dimension, which is strictly speaking the RFOT, has been proposed.

In a first section we will give the original Adam and Gibbs argument. We will show in a (long) second section how this idea finds their microscopic supports within a mean-field perspective. In the third and last section we will present what we think to be a good scenario for a finite-dimension description.

3.1 Adam-Gibbs argument

How to understand the dynamical slowing down close to T_g ? As it has been already discussed in the first chapter, a plausible explanation is to introduce

a rough (free) energy landscape. : in this complex topology, the system could be trapped, on rather short times, in a local potential minimum, and only relax, on the long time scales, by jumping from a minimum to an other one. This picture is experimentally supported by two main facts : i) the existence of an excess entropy, ii) the extrapolated Kauzmann temperature T_K is remarkably close to the temperature T_0 extrapolated from time Vogel-Fulcher like fits.

So, let us to assume, in the super-cooled phase, the existence of some amorphous clusters specified by a given linear size ξ, what Adam and Gibbs called *cooperative rearranging regions*. Moreover, we state that relaxation time is determined by some global cooperative move of this cluster, that is :

$$\tau \propto e^{\beta \xi^d} \tag{3.1}$$

In this scheme, it is quite natural to see excess entropy as a configurational entropy, that is related to the number of preferred amorphous states, and to write :

$$\mathcal{N}_{amorphous} \propto e^{S_c(T)V} \tag{3.2}$$

$$\propto \mathfrak{f}^{\frac{V}{\xi^d}} \tag{3.3}$$

V being the volume of the system and $\mathfrak{f}$ the number of "good" configurations. Using this last relation,

$$\tau \propto e^{\beta \frac{\ln \mathfrak{f}}{S_c(T)}} \tag{3.4}$$

And from the fact that, from experiments,

$$S_c(T) \propto \frac{T - T_K}{T_K^2} \tag{3.5}$$

We obtain the desired Vogel-Fulcher law for the relaxation time, and the identification of T_0 and of T_K. But this phenomenological argument raises some question :

- Where does the typical length ξ come from ? How to compute $\mathfrak{f}$? In other words, we ask for a microscopic derivation.
- Why $\tau \propto e^{\beta \xi^d}$? This relation assume that a finite fraction of the clusters should relax cooperatively, that is the worst case in terms of relaxation.

- Measurements have shown that $\xi = \left(\frac{\ln \mathfrak{f}}{S_c(T)}\right)^{1/3}$ grows too slowly to explain a drastic arrest of the dynamics.

All this limitatins have led to the building of the RFOT.

3.2 A mean-field theory : statics and dynamics

3.2.1 Existence of an entropy-vanishing transition : the random energy model.

The first example of entropy vanishing model is the well-known random energy model (REM) [10, 11]. This model was early introduced by Derrida as an idealization of a spin-glass model. It was later understood this model does not belong to the spin-glass universality class.

The definition of this model is the following : we consider the 2^N configurations of N Ising spins, and we assume that the energy of each configuration is an independent Gaussian random variable of null mean and variance equal to $\frac{N}{2}$.

The quantities of interest, as usual in the context of disordered systems, are those verifying the property of self-averaging, that is to say the fact a quantity is equal to its disorder averaged mean value in the thermodynamic limit. The free energy is one of this quantities, the partition function is not. So we shall average $\ln Z$ with respect to the disorder distribution. This can be done by using an integral representation of the logarithm.

In the following, we use another strategy. Let us consider the density of states defined as the number of states being in the interval $[E, E + dE]$:

$$\rho(E) = \sum_{\mathfrak{C}} \delta(E - E_{\mathfrak{C}}) \tag{3.6}$$

A straightforward computation show that :

$$\overline{\rho(E)} = \frac{2^N}{\sqrt{\pi N}} e^{-\frac{E^2}{N}} \tag{3.7}$$

$$\overline{\rho(E)\rho(E')} = \overline{\rho(E)}\ \overline{\rho(E')} + \overline{\rho(E)} \left(\delta(E - E') - \frac{e^{-\frac{E'^2}{N}}}{\sqrt{\pi N}} \right) \tag{3.8}$$

Correlations of $\rho(E)$ are negligible as long as the entropy is positive. Indeed, recalling that in the micro-canonical ensemble, the entropy is given by $NS(E) = \ln \rho(E)$. We have the following results for the REM :

$$S(E) = \frac{1}{N}\overline{\ln \rho(E)} = \frac{1}{N} \ln \overline{\rho(E)} \tag{3.9}$$

$$= \ln 2 - \left(\frac{E}{N}\right)^2 \tag{3.10}$$

The entropy vanishes at $E = \pm N\sqrt{\ln 2}$. As REM is a discrete model, the entropy can not become negative : its cancellation is the signature of a phase transition. Turning back to the partition function,

$$Z = \sum_{\mathfrak{C}} e^{-\beta E_{\mathfrak{C}}} \tag{3.11}$$

$$= \sum_{\mathfrak{C}} e^{-\beta E_{\mathfrak{C}}} \int dE \delta(E - E_{\mathfrak{C}}) \tag{3.12}$$

$$= N \int dee^{N(S(e)-\beta e)} \tag{3.13}$$

where we have introduced the energy per spin e. The free energy is then given by

$$-\beta \frac{F}{N} = \frac{1}{N} \ln Z \tag{3.14}$$

$$= \max_e [S(e) - \beta e] \tag{3.15}$$

where the saddle point $e^*(\beta)$ shall verify :

$$\beta = \frac{\partial S}{\partial e}|_{e^*} \ (T > T_c) \tag{3.16}$$

We have plotted the condition on the saddle point value of the free energy and the entropy of the REM on the figure (3.1). The critical temperature is then given by : $T_c = \frac{1}{2\sqrt{\ln 2}}$. Using equation (3.16), as long as $T > T_c$,

$$e(T) = -\frac{1}{2T} \tag{3.17}$$

$$C(T) = \frac{1}{2T^2} \tag{3.18}$$

$$S(T) = \ln 2 - \frac{1}{4T^2} \tag{3.19}$$

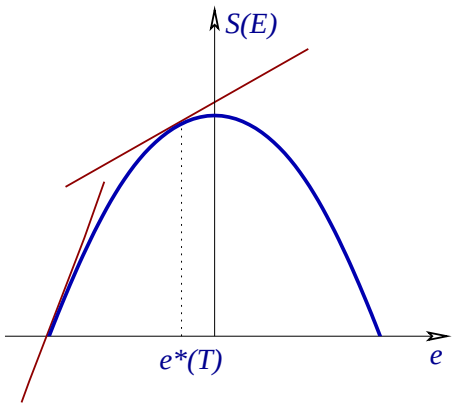

Figure 3.1: Entropy and free energy in th REM model

And below T_c,

$$e(T) = -\sqrt{\ln 2} \tag{3.20}$$
$$C(T) = 0 \tag{3.21}$$
$$S(T) = 0 \tag{3.22}$$

Link with liquids & universality

The gross phenomenology of the REM is reminiscent of super-cooled liquids one. However, in the liquid case, only some degrees of freedom are frozen at T_K : the specific heat decreases at $T < T_g$, it would be null only if all degrees were frozen. REM is not the unique example of a model having this kind of transition. It belongs to a broad class of models (the 1-RSB ones, we postpone this discussion to the next sections). Among them let us mention the lattice glass model or the p-spin model.

Lattice glass model [20] is defined as follow : there is one particle or less per site, each particle having an infinite energy if it has more than m neighbors, a null energy otherwise. This model does not share anything in common with the Kob-Andersen model : in the lattice glass there is no dynamical rules but thermodynamic ones on the energies.

A drawback of the simplicity of the REM is that there is no dynamical transition as in other 1-RSB models.

3.2.2 A spin analogy to glass transition

The p-spin model [13, 23] is defined as follow :

$$H = -\sum_{i_1<\ldots<i_p} J_{i_1\ldots i_p} S_{i_1}\ldots S_{i_p} \tag{3.23}$$

where the couplings are independant identically distributed Gaussian random variables, the normalization of the couplings is chosen in order to preserve extensivity of the free energy :

$$\overline{J_{i_1\ldots i_p}} = 0 \tag{3.24}$$

$$\overline{J^2_{i_1\ldots i_p}} = \frac{p!}{2N^{p-1}} \tag{3.25}$$

In the p-spin models, the N spins could be either Ising spins or continuous variables satisfying the spherical constraint ($\sum_i S_i^2 = N$). Like in the REM, the energies $E_{\mathfrak{C}}$ are (as sums of Gaussian variables) Gaussian random variables, but they are no more independent :

$$\overline{E^2_{\mathfrak{C}}} = \sum_{i_1<\ldots<i_p} \sum_{l_1<\ldots<l_p} \overline{J_{i_1\ldots i_p} S_{i_1}\ldots S_{i_p} J_{l_1\ldots l_p} S_{l_1}\ldots S_{l_p}} \tag{3.26}$$

$$= \frac{N}{2} \tag{3.27}$$

$$\overline{E_{\mathfrak{C}^a} E_{\mathfrak{C}^b}} = \sum_{i_1<\ldots<i_p} \overline{J^2_{i_1\ldots i_p} S^a_{i_1}\ldots S^a_{i_p} S^b_{l_1}\ldots S^b_{l_p}} \tag{3.28}$$

$$= \frac{N}{2}\left(\frac{1}{N}\sum_i S_i^a S_i^b\right)^p \tag{3.29}$$

$$\equiv \frac{N}{2} q_{ab}^P \tag{3.30}$$

q_{ab} is a measure of the overlap between configurations a and b. This a function taking its value in $[-1 : 1]$, consequently, when p tends to ∞, the correlations vanish except in the case $\mathfrak{C}^a = \mathfrak{C}^b$. In this limit p-spin is nothing but the REM. In fact, already for $p \geq 3$, p-spin belongs to the same universality class as the REM.

The Thouless Anderson Palmer approach

The idea of the TAP approach [7, 15, 17]is to perform a Legendre transform, that is to introduce a free energy, F_{TAP}, function of the local magnetizations

$m_i's$:

$$-\beta F_{TAP} = \ln \sum_{\mathfrak{C}=S_1...S_N} e^{-\beta H(\mathfrak{C})-\sum_i h_i(S_i-m_i)} \tag{3.31}$$

where the fields h_i are chosen to satisfy $< S_i >= m_i$, the notation $< . >$ meaning the thermodynamic average with respect to the weight $\frac{e^{-\beta H(\mathfrak{C})}}{Z}$. We are interested by the minima of F_{TAP}. They represent the thermodynamic states, the stable and the unstable ones. They are given by :

$$\frac{\partial F_{TAP}}{\partial m_i}|_{h_i \to 0} = 0 \tag{3.32}$$

As an exercise, one can derive TAP equations for the fully connected Ising model, and obtain again the self-consistent equation on the magnetization (the Curie-Weiss equation).

The derivation of the TAP function in the p-spin case needs to take into account a reaction term, known as Onsager reaction term. Introducing $q \equiv \frac{1}{N}\sum m_i^2$, one finds for example for the spherical version,

$$F_{TAP} = -\sum_{i_1<...<i_p} J_{i_1...i_p} m_{i_1}...m_{i_p} - \frac{1}{2\beta}\ln(1-q) - \frac{\beta}{4}[(p-1)q^p - pq^{p-1} + 1]$$

And finally the number of solutions of the TAP equation $\mathcal{N}(f)$ would be obtained by computing :

$$\begin{aligned} \mathcal{N}(f) &\equiv \int \prod_i dm_i \delta(\frac{\partial F_{TAP}}{\partial m_i})|\det(\frac{\partial^2 F_{TAP}}{\partial m_i \partial m_j})|\delta(F[m_i] - Nf) \quad (3.33) \\ &\propto e^{NS_c(f)} \quad (3.34) \end{aligned}$$

The precise study of $S_c(f)$ [23] show the existence of two temperatures : i) an upper one, called temperature of threshold or T_d, above which, there is only one (paramagnetic) solution of the TAP equations contributing to the partition function ii) a second one known has T_K where there is an infinite number of solutions of TAP equation, but no more an exponential one. That is the true static transition.

Moreover, the stability of these solutions are governed by the threshold temperature. A detailed diagonalization of the stability matrix $M_{ij} = \frac{\partial^2 F_{TAP}}{\partial m_i \partial m_j}$ [8] has shown that its spectrum is given by a Wigner semi-circle law whose support is strictly positive for $T < T_d$. T_d is the temperature where marginally stable directions appear and the states lose their stability.

The solution α of the TAP equations, having the TAP energy $F(m_i^\alpha) \equiv F_\alpha$, are therefore the dominating configurations of the partition function :

$$Z = \sum_\alpha e^{-\beta F_\alpha} \tag{3.35}$$

$$= \int df \mathcal{N}(f) e^{-\beta N f} \tag{3.36}$$

$$= \int df e^{N(-\beta f + S_c(f))} \tag{3.37}$$

The discussion reminds the case of the REM (see figure (3.2)), with free en-

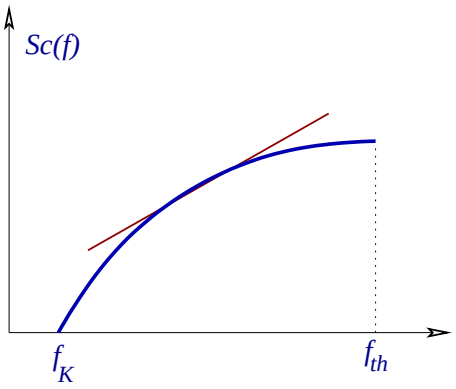

Figure 3.2: Configurational entropy $S_c(f)$

ergy replacing energy, configurational entropy entropy. But we can be more precise : T_d plays the role of a spinodal, when $T_K < T < T_d$, metastable states appear trapping the system for a time given by the heights of activation barriers. Because of these metastable states we expect a dynamical slow down at T_d. We should add that in a mean-field model like p-spin, the height of the barriers grows like N : the slow down becomes a dynamical arrest in the thermodynamic limit ; there is an ergodicity breaking at T_d.

Langevin dynamics of the spherical p-spin

The Langevin dynamics of the p-spin spherical model could be solved thanks to the generating functional method [7, 23]. The key point is that p-spin is a fully-connected (mean-field) model. We just want to illustrate the main

steps of this derivation. We start from, $\mu(t)$ being the dynamical spherical constraint (fixed so that $< \sum_i S_i^2 >= N$) :

$$\partial_t S_i(t) = -\frac{\delta}{\delta S_i} H - \mu(t) S_i(t) + \eta_i(t) \quad (3.38)$$

$$< \eta_i(t)\eta_j(t') > = 2T\delta(t-t') \quad (3.39)$$

The starting point of the method is the naive identity (by using the Ito prescription to have an equation Jacobian equal to one) :

$$1 = \int DS_i(t) D\eta_i(t) P(\eta_i) \delta(\partial_t S_i(t) + \frac{\delta}{\delta S_i} H + \mu(t) S_i(t) - \eta_i(t)) \quad (3.40)$$

Introducing an exponential representation of the Dirac distribution and so the auxiliary fields $\hat{S}_i(t)$,

$$1 = \int DS_i(t) D\eta_i(t) e^{\mathcal{S}(S_i, \hat{S}_i)} \quad (3.41)$$

This expression is averaged with respect to the disorder, by noting that $\mathcal{S}(S_i, \hat{S}_i)$ can be split into one part independent from the disorder distribution, linearly dependent of the couplings. Performing this average, we are introducing three non-null dynamical quantities which are nothing else than the dynamical overlap or correlation C(t,t') and the response functions R(t,t') and R(t',t).

$$C(t,t') \equiv \frac{1}{N} \sum_i S_i(t) S_i(t') \quad (3.42)$$

$$R(t,t') \equiv \frac{\delta}{\delta h_i(t')} < S_i(t) >=< S_i(t) \hat{S}_i(t') > \quad (3.43)$$

By using identities on correlation and response functions in this field theoretic framework, and using the spherical constraint, one obtains an equation for the correlation function :

$$\partial_\tau C(\tau) = -TC(\tau) - \frac{p}{2T} \int_0^\tau du C^{p-1}(\tau - u) \partial_u C(u) \quad (3.44)$$

A detailed study of this *exact* equation shows that :

- the correlation has the expected behavior :
  1. a short-time dynamics with a power-law approach to the developing plateau

2. a long-time dynamics with a power-law departure from the plateau

- *there exists a dynamical temperature* T_d, the same as in the TAP approach, below which an infinite plateau arises in the correlation function, *i.e.* below which the system never relaxes. This lack of ergodicity can be studied as a critical phenomenon : one can prove that the relaxation time grows like $|T - T_d|^{-\gamma}$.
- the static overlap, *i.e.* the infinite-time limit of the correlation function, jumps discontinuously from 0 to a finite value across T_d with a singularity proportional to $|T - T_d|^{1/2}$

3.2.3 Link to the theory of liquids : Some words on universality.

Some words on the mode-coupling theory (MCT)

The mode-coupling theory is a completely independent theory derived from Newton laws of motion through the projection operator formalism. The main achievement of MCT is to derive a self consistent equation on the density-density correlations. Let us introduce :

$$F(\overrightarrow{q},t) \equiv \frac{1}{N}\sum_{k,l} e^{i\overrightarrow{q}[\overrightarrow{r}_k(t)-\overrightarrow{r}_l(0)]} \quad (3.45)$$

$$= \mathcal{FT}[<\delta\rho_x(t)\delta\rho_y(0)>] \quad (3.46)$$

One obtains the general equation :

$$\partial_{tt}F(q,t) + \frac{q^2T}{F[q,0]}F(q,t) + \int_0^t dt'[M_0(q,t-t') + M(q,t-t')]\partial_{t'}F(q,t') = 0$$

The kernel M_0 is related to the short-time dynamics : this term reduces to a friction term $M_0(q,t-t') = \nu\delta(t-t')$. The second kernel M is in the mode-coupling approximation given by :

$$M(q,t) = \frac{\rho T}{16\pi^3 m}\int dk|V_{q-k,k}|^2F(k,t)F(q-k,t) \quad (3.47)$$

$$V_{q-k,k} = \frac{\lambda}{\rho_0}[(1-\frac{1}{F(k,0)})\hat{q}.\overrightarrow{k} + (1-\frac{1}{F(q-k,0)})\hat{q}.(\overrightarrow{q}-\overrightarrow{k})] \quad (3.48)$$

where $\hat{q} = \frac{\overrightarrow{q}}{\|\overrightarrow{q}\|}$. The predictions of MCT for the correlation are strictly identical to the p-spin case. The true reason is hidden in the last equations.

If one does the naive, but quite reasonable, approximation that the structure factor $S(q) = F(q, 0)$ is centered around a vector q_0, *e.g.* the inverse of the typical space between a particle and its first neighbors, in the over-damped limit ($\partial_{tt}F(q,t) = 0$), one can write :

$$\nu\partial_t F(q,t) + \frac{q^2 T}{F[q_0,0]}F(q,t) + \lambda\int_0^t dt' F^2(q_0, t-t')\partial'_t F(q_0,t') = 0 \quad (3.49)$$

which is strictly identical to the equation (3.44) for the spin-spin correlation. This is called the schematic approximation.

Recent developments have allowed to rephrase the MCT in a field theoretic perspective. It appears that this theory is a self-consistent approximation at one-loop of the self-energy. Although the inclusion of the fluctuation-dissipation theorem remains delicate, this framework has revealed the landau-like nature of this theory : to each order of the complete diagram expansion the theory remains stable above the upper critical dimension [2]. We consider in that sense the MCT theory as a "mean-fieldish" theory, in the sense it does take into account activated events, instantons,...

On the universality of p-spin-MCT transition

The universality of this transition relies on the so-called one-step replica symmetric breaking (1-RSB) nature of the static transition of the p-spin. We want to show the link with the Parisi replica theory [18]. The idea is similar to the description of a spinodal point. In the temperature range $[T_K, T_d]$, the stable phase is the paramagnetic one. However, to take into account the presence of metastable states we use the low-temperature solution (the 1-RSB solution), which is only stable at $T < T_K$. But as there is no spontaneous symetry breaking in the temperature range $[T_K, T_d]$, one has to add a field to enforce some explicite symetry breaking.

To do this, we coupled m replicas of the system by a small pinning field of strength ϵ, that is if we sum over the states of these replicas :

$$Z^m = \sum_{\alpha_1 \ldots \alpha_m} e^{-\beta(\mathrm{f}_{\alpha_1} + \ldots + \mathrm{f}_{\alpha_m}) + \epsilon \sum_{a \neq b} g(q_{\alpha_a \alpha_b})} \quad (3.50)$$

There will be a competition between the pinning field and the entropy understood here as the number of states like in the TAP approach. Thus, there exists a critical value for ϵ above which the replicas are coupled, and below which they are completely independent that is of null overlap.

Suppose we go across the transition from the higher values of ϵ, we have to take into account the existence of numerous metastable states of replicas becoming uncoupled :

$$Z^m = \left(\sum_\alpha e^{-N\beta \mathfrak{f}_\alpha} \right)^m \tag{3.51}$$

$$= \left(\int d\mathfrak{f}\ e^{-N[\beta \mathfrak{f} + S_c(\mathfrak{f})]} \right)^m \tag{3.52}$$

The free energy per spin for each replica is now :

$$f \equiv \frac{1}{mN} \ln Z^m = -\beta \mathfrak{f}_u + S_c(\mathfrak{f}_u) \tag{3.53}$$

And saddle-point equation is given by :

$$\beta = \frac{\partial S_c}{\partial \mathfrak{f}}|_{\mathfrak{f}_u} \tag{3.54}$$

Both equations are m-independent.

Now, let us do the same computation for the coupled replica solution, that is for replica having the same states. We have :

$$Z^m_{coupled} = \sum_\alpha e^{-Nm\beta \mathfrak{f}_\alpha} \tag{3.55}$$

$$= \int d\mathfrak{f}\ e^{-N[\beta m \mathfrak{f} + S_c(\mathfrak{f})]} \tag{3.56}$$

The saddle-point condition becomes :

$$m\beta = \frac{\partial S_c}{\partial \mathfrak{f}}|_{\mathfrak{f}_c} \tag{3.57}$$

Its solution depends on m and consequently the free energy too,

$$f \equiv \frac{1}{mN} \ln Z^m_{coupled} = -\beta \mathfrak{f}_c + \frac{1}{m} S_c(\mathfrak{f}_c) \tag{3.58}$$

In the limit m tending to one,

$$\frac{d}{dm} \frac{\ln Z_{coupled}}{mN}|_{m \to 1} = -S_c(\mathfrak{f}_c) \tag{3.59}$$

There is a remarkable balance between the free energy of states and their number. This is the way to do approximate computations in finite dimension ; TAP approach becomes too cumbersome.

Let us turning to the Parisi theory. In this theory we have to evaluate :

$$\frac{1}{N}\overline{\ln Z_{Parisi}} = \lim_{n\to 0}\frac{\overline{Z^n_{Parisi}}}{n} \tag{3.60}$$

Z^n is easily evaluate when n is an integer. Without any kind of mathematical justification we will take the analytical continuation in order to perform the limit n tends to 0. In the p-spin case, introducing $Q_{ab} = \frac{1}{N}\sum_i S_i^a S_i^b$, one gets :

$$\overline{Z^n_{Parisi}} = \int dQ_{ab} e^{N\left[\frac{\beta^2}{4}\sum_{ab} Q_{ab}^p + S(Q_{ab})\right]} \tag{3.61}$$

Where the term $S(Q_{ab})$ is an entropy-like term that can be computed, its shape depends whether the S_i's are Ising spins or spherical spins. To achieve the computation, we have to parameterize the $n \times n$-matrix Q.The simplest choice for Q_{ab} is to take :

$$\begin{pmatrix} 1 & 0 & 0 & ... & 0 & 0 \\ 0 & 1 & 0 & ... & 0 & 0 \\ & & & ... & & \\ 0 & 0 & 0 & ... & 0 & 1 \end{pmatrix} \tag{3.62}$$

One can show that this choice means that all replicas are uncoupled.This solution leads to a vanishing entropy at a certain temperature. The computation of the saddle-point for the coupled replica phase shall be done thanks to the 1-RSB Parisi Ansatz :

$$\begin{pmatrix} 1 & q & 0 & 0 & ... & 0 & 0 \\ q & 1 & 0 & 0 & ... & 0 & 0 \\ & & & ... & & & \\ 0 & 0 & 0 & ... & 0 & q & 1 \\ 0 & 0 & 0 & ... & 0 & q & 1 \end{pmatrix} \tag{3.63}$$

This Ansatz means that we consider the case, writing $n = m \times l$, of $m \times l$ replicas coupled if they are inside the same cluster of m replicas, uncoupled otherwise. One can see that the analytic continuation forces m to be lower than 1. In the Parisi theory, the replica symmetry breaking is spontaneous

: there is no need to add a pinning field ϵ. But to obtain the saddle-point we have to maximize upon q, and also upon m. The condition on m is quite unclear.

The pinning field shows that the optimization condition on m in the Parisi theory is nothing else that the vanishing of the configurational entropy.

$$\frac{d}{dm}\frac{\ln \overline{Z^m_{coupled}}}{m} = \frac{d}{dm}\ln \overline{Z^n_{Parisi}} = -S_c(\mathfrak{f}^*) = 0 \tag{3.64}$$

There is a spontaneous symmetry breaking. One sees thanks to this argument that the p-spin dynamical transition relies completely on the existence of a static 1-RSB transition. This gives to this transition the universality of the 1-RSB transition.

3.3 A finite dimension extension : the mosaic states

To include activated events, and so to have a finite-dimension theory, we need to make the link between the real space and the rough free energy landscape. The common path is to use fluctuation-dissipation theorem. By noting that at equilibrium :

$$\frac{\partial^2}{\partial m_i \partial m_j} F = \frac{\partial}{\partial m_i} h_j \tag{3.65}$$

$$= [< S_i S_j >_c]^{-1} \tag{3.66}$$

So the appearance of flat direction in the stability matrix leads to long range correlations, but these correlations are extremely oscillating. A more appropriate object is G_4. Recalling that :

$$G_4 =< S_x(t) S_y(t) S_x(0) S_y(0) >_c \tag{3.67}$$

In the plateau part for, a temperature slightly above T_d, the system remains for a long time in a fixed state before relaxing. During this time, the system does not explore other states, we can write :

$$G_4 \simeq < S_x(t) S_y(t) >< S_x(0) S_y(0) > \tag{3.68}$$

$$\simeq \overline{< S_x S_y >^2_\alpha}^\alpha \tag{3.69}$$

The existence of a long range order could also be seen in G_4. But for times of order of the relaxation time τ_α, we really have to study the dynamics,

which can be done for example thanks to the MCT. It has been shown that for example that :

$$\xi_{MCT} \propto |T - T_d|^{-\frac{1}{4}} \tag{3.70}$$
$$\tau_\alpha \propto |T - T_d|^{-\gamma} \tag{3.71}$$
$$\chi_4 \propto |T - T_d|^{-1} \tag{3.72}$$

This suggests a dynamical phase transition at T_d. Instead, in real systems, there is a cross-over. The relaxation time do not diverge in finite dimension at T_d. Why so ?

Fragility of thermodynamic states in finite dimension

In order to test the mean-field scenario, we assume that true thermodynamic states exist in finite dimension. We can do the following gedanken experiment : we freeze the particle in the state α, with $\mathfrak{f}_\alpha = \mathfrak{f}^*$ outside a sphere $\mathcal{B}_R$ of radius R, and let them evolve inside. Let us rewrite the partition function :

$$Z = \sum_{\gamma \in \mathcal{B}_R, \gamma \neq \alpha} e^{-\beta \mathfrak{f}_\gamma R^d} + e^{-\beta \mathfrak{f}_\alpha R^d + \beta \Upsilon R^\theta} \tag{3.73}$$

where $\beta \Upsilon R^\theta$ is a free-energy gain due to the matching between the state α and the configurations outside, so that $\theta \leq d-1$. Introducing the configurational entropy of states of the sphere :

$$Z = \int d\mathfrak{f} e^{R^d(-\beta \mathfrak{f} + S_c(\mathfrak{f}))} + e^{-\beta \mathfrak{f}_\alpha R^d + \beta \Upsilon R^\theta} \tag{3.74}$$
$$= e^{-\beta \mathfrak{f}^* R^d} \left[e^{-S_c(\mathfrak{f}^*) R^d} + e^{\beta \Upsilon R^\theta} \right] \tag{3.75}$$

From the last expression, emerges a natural length $\xi^* = \left(\frac{\Upsilon}{T S_c(T)} \right)^{\frac{1}{d-\theta}}$, which diverges when $S_c(T)$ vanishes at T_K. If the radius of the sphere is lower than ξ^*, boundary condition fix the inside of the sphere in the state α, otherwise, configurational entropy fixes it to an other state.

Mosaic states

The picture emerging from this instability of thermodynamic states in finite dimension is referred as mosaic states [22]. The main hypothesis is that

the system is in its mean-field states on scales $l < \xi^*$, and can be thought as a mosaic of mean-field patches of typical size ξ^* on larger scales. The relaxation is then given by :

$$\tau \propto e^{K\beta\xi^{*\psi}} = e^{K\beta\left(\frac{\Upsilon}{TS_c(T)}\right)^{\frac{\psi}{d-\theta}}} \tag{3.76}$$

$$= e^{K\left(\frac{c}{T-T_K}\right)^{\frac{\psi}{d-\theta}}} \tag{3.77}$$

The most naive choice of the exponents is $\psi = \theta = d-1$. But, to obtain the experimental Vogel-Fulcher law, this for sure is not the good choice. Some authors argue that $\psi = \theta = \frac{3}{2}$, but the arguments behind this assumption are far from being widely accepted.

Note these results are not exactly similar to the Adam-Gibbs argument, thought there is a clear similarity. If in the two cases, the divergence of the time scales is due to a vanishing entropy, the precise dependence on $S_c(T)$ is different. The RFOT picture seems quite heuristic, but it has recently found a microscopic support with the introduction of Kač p-spin. The first instantonic computations suggest however $\theta = d-1$.

Some numerical test have also been performed on soft spheres reproducing the gedanken experiment of fragmentation. By measuring the evolution with the sphere radius of the overlap q of the inside of the sphere with the frozen external state, one would expect a sharp decrease of q around ξ^*. Unfortunately, only a rather smooth decrease has been observed [1]. The very reason of such an effect is not completely understood at the present moment. One likely possibility is that the generalized surface tension Υ fluctuate from state to state.

A strange feature of the mosaic states picture is that the correlation length is here a static one. This is a very subtle one, since it is the correlation of the center of the sphere with the set of the points at the surface of the sphere. This is a new kind of static correlation length.

As a conclusion on mosaic states let us summing up the present situation :

- This theory take into account i) all the MCT results and also ii) the relations between Vogel-Fulcher fits and excess entropy extrapolations. That is to say both the mean-field theory and the activated events.
- But some points remain obscure :
    1. The comparison with numerics is encouraging, but different points remain to be explained.

2. A microscopic derivation of θ, ψ, Υ ... is deeply needed.
3. The link between ξ^* and ξ_4 is still unclear.
4. The precise definition of what we mean by state, their geometry (fractals ?) has to be determined.

Chapter 4

Slow dynamics and Aging

We send back the reader to a course written by G.Biroli [12]

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