CHAPTER 1

FIRST STEPS IN GLASS THEORY

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1.1 INTRODUCTION

When quenched fast enough, so that it avoids the crystallization transition, almost any liquid becomes a glass [1]. This means that the density profile is not flat as in a liquid. It contains some peaks as in a crystal, but the peaks are not located on the nodes of a periodic or quasi-periodic lattice. The understanding of such amorphous 'solid' states has been recognized for a long time to be a major question in Condensed Matter Physics. The sentence by Phil Anderson "... there are still fascinating questions of principle about glasses and other amorphous phases..." [2], written nearly thirty years ago, was once again visionary in that it foresaw the wonderful developments in glassy systems, especially spin glasses. The progress in these areas has been difficult, particularly in the study of structural glasses.

1.2 MATHEMATICS

The first question that comes to mind is whether the glass is a new state of matter. It is not distinguished by any obvious symmetry (a non-obvious symmetry will be discussed later) from the liquid state, and one might think (as many people do) that the density profile should actually become flat on time scales longer than the experimental ones: the glass is just a liquid with a long relaxation time.

From the statistical physics point of view, one wants to start from a microscopic Hamiltonian. The simplest situation is that of N point-like particles in a volume V, with a pair-interaction potential

$$H = \sum_{i<j} V_{ij}(r_i - r_j). \tag{1.1}$$

A simple case is a homogeneous system in which V_{ij} is, for instance, either a hard-sphere potential, a 'soft-sphere' potential ($V_{ij}(r) = A/r^{12}$), or a Lennard-Jones potential ($V_{ij}(r) = A/r^{12} - B/r^6$). Another system that is much-studied numerically (because crystallization is more easily avoided) are the binary mixtures with two types of particles [3]: particle i has $\epsilon_i \in \{\pm 1\}$ and $V_{ij}(r) = V_{\epsilon_i \epsilon_j}(r)$, where V_{++}, V_{--}, and $V_{+-} = V_{-+}$ are three potentials of the same type as before, but with different A and B parameters corresponding to particles $+$ and $-$ with different radii.

Does there exist, in any such case, an independent state of matter which is the glass state? Does it exist as a long-lived metastable state (like the diamond phase of carbon)? Nobody knows the rigorous mathematical answer to these questions. Actually, simpler related questions remain unanswered (e.g. proving the existence of a spin-glass phase in a finite dimensional short range system [4]). Others have only been solved after great effort (e.g. proving Kepler's conjecture that the densest three dimensional packing of hard spheres is the fcc/hcp lattice [5]).

1.3 EXPERIMENTS

Experimentally, the liquid falls out of equilibrium on experimental time scales and becomes a 'glass' at a temperature T_g called the glass temperature [1]. This glass temperature is conventionnally defined as the one at which the relaxation time τ of the liquid, as obtained e.g. from viscosity or from susceptibility measurements, becomes of the order of 10^3 seconds. Angell's plot of $\log(\tau/1s)$ versus T_g/T allows us to distinguish several types of behavior (fig. 1.1). So-called strong glasses like SiO_2 have a typical Arrhenius behavior with one well-defined free energy barrier. On the other hand, some glasses, called fragile, show a dramatic increase of the relaxation time with decreasing temperature T that is much faster than Arrhenius: the typical free energy barrier thus increases when T decreases. This implies a collective behavior involving more and more particles. An increase of the dynamic correlation, characteristic of the mobile particles (rather than the more natural correlation of frozen particles), has been found in recent simulations [7]. A popular fit of the relaxation time versus T is the Vogel-Fulcher rule,

$$\tau \sim \tau_0 \exp\left(\frac{A}{T - T_{VF}}\right) \tag{1.2}$$

which would predict a phase transition at a temperature T_{VF} that is not accessible experimentally (while staying at equilibrium). The more fragile the glass, the closer is T_{VF} to T_g, while strong glass formers have a T_{VF} close to zero.

Another interesting experimental signature is that of the specific heat. When one cools the liquid slowly, at a cooling rate $\Gamma = -dT/dt$, it freezes into a glass at a temperature that decreases slightly when Γ decreases. When this freezing occurs, the specific heat jumps downward, from its value in the equilibrated supercooled liquid state to a glass value that is close to that of the crystal. From the specific heat, one can compute the entropy. The configurational entropy,

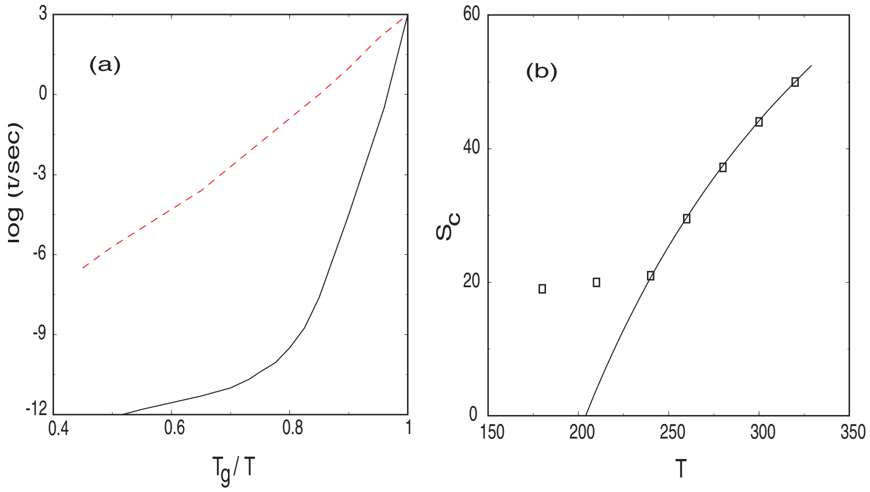

Figure 1.1: The left-hand figure (a) shows the behavior of the logarithm (to base 10) of the relaxation time in seconds, versus T_g/T, for two extreme cases of glass formers. The dashed line represents GeO_2, a strong glass former displaying Arrhenius-like behavior. The full line is the measurement from OTP, which is a fragile glass former with a relaxation time that diverges much faster than the Arrhenius law. The right-hand figure (b) shows the configurational entropy S_c of OTP (in JK^{-1}/mol) versus T. The configurational entropy, defined as the difference between the entropy of the supercooled liquid and that of the crystal, is measured through an integral of the specific heat difference. The squares are the experimental values. The glass temperature is T_g = 246 K. The full line is a fit to the equilibrated data, of the type $S_c = S_\infty(1 - T_K/T)$. The Kauzmann temperature is T_K = 204 K, while the fusion temperature is 331 K. The data are taken from [6].

defined experimentally as the difference $S_c = S_{liq} - S_{crystal}$, behaves smoothly in the supercooled liquid phase, until the system becomes a glass (see fig.1.1). It was noted by Kauzmann long ago that, if extrapolated, $S_c(T)$ vanishes at a finite temperature T_K. If cooled more slowly, the system follows the smooth $S_c(T)$ curve down to slightly lower temperatures, but then freezes again. One can wonder what could happen at infinitely slow cooling. As a negative S_c does not make sense (except for pure hard spheres, where there is no energy), something must happen at $T > T_K$. The curve $S_c(T)$ could flatten down smoothly, or there might be a phase transition, which in the simplest scenario would lead to $S_c(T) = 0$ at $T < T_K$. This idea of an underlying 'ideal' phase transition, which could be obtained only at infinitely slow cooling, receives some support from the following observation: the two temperatures T_{VF} and T_K, at which the *extrapolated* experimental behavior has a singularity, turn out to be amazingly close to each other (see the table below) [6]. The first phenomenological attempts to explain this fact were by Kauzmann [8]. They were further developed by, among others, Adam, Gibbs and Di-Marzio [9], who identified the glass transition as a 'bona fide' thermodynamic transition blurred by some dynamical effects.

If there exists a true thermodynamic glass transition at $T = T_K = T_{VF}$, it is a transition of a strange type. On the one hand, it is of second-order because the entropy and internal energy are continuous. On the other hand, the order parameter is discontinuous at the transition, as in first-order transitions: the modulation of the microscopic density profile in the glass does not appear continuously from the flat profile of the liquid. As soon as the system freezes, there is a finite jump in this modulation (A more precise definition of the order parameter is given below).

Comparison of T_K and T_{VF} in various glass-formers (from [6])

Substance	$T_K(K)$	$T_{VF}(K)$	$T_g(K)$
o-terphenyl	204.2	202.4	246
salol	175.2		220
2-MTHF	69.3	69.6	91
n-propanol	72.2	70.2	97
3-bromopentane	82.5	82.9	108

1.4 A MEAN-FIELD SPIN-GLASS ANALOGY

A totally different class of systems in which a similar 1st- to 2nd-order type of transition was found, and studied in great detail, is a certain category of mean-field spin glasses. A few years after the replica symmetry breaking (RSB) solution of the mean-field theory of spin glasses [10], it was realized that there exists another category of mean-field spin glasses in which the static phase transition exists and is due to an entropy crisis [11]. These are now called discontinuous spin glasses because their phase transition has a discontinuous order parameter, despite being second-order in the Ehrenfest sense [12]. Another name often found in the literature is 'one-step RSB' spin glasses, because of the special pattern of symmetry breaking involved in their solution. These are spin glasses with infinite-range interactions involving a coupling between triplets (or higher order groups) of spins. The simplest among them is the random-energy model, which is the

$p \to \infty$ limit version of the p-spin models described by the Hamiltonian

$$H = - \sum_{i1<\ldots<i_p} J_{i_1\ldots i_p} s_{i_1} \ldots s_{i_p}, \tag{1.3}$$

where the J's are (appropriately scaled) quenched random couplings, and the spins can be either of Ising or spherical type [12, 13, 14].

The analogy between the phase transition of discontinuous spin glasses and the thermodynamic glass transition was first noticed by Kirkpatrick, Thirumalai and Wolynes in a series of inspired papers of the mid-eighties [13]. While some of the basic ideas of the present development were around at that time, a few crucial ingredients were still missing. On the one hand, one needed to get more confidence that this analogy was not just fortuitous. The big obstacle was the existence (in spin glasses) versus the absence (in structural glasses) of quenched disorder. The discovery of discontinuous spin glasses without any quenched disorder [15, 16, 17] provided an important new piece of information: contrary to what had long been believed, quenched disorder is not necessary for the existence of a spin glass phase (but frustration is).

It is important to analyze critically this analogy from the point of view of the dynamical behavior. In discontinuous, mean-field spin glasses, there exists a 'dynamical transition' temperature T_c that is higher than the equilibrium transition T_K. When T decreases and approaches T_c, the correlation function relaxes with a characteristic two-step form: a fast β-relaxation leading to a plateau takes place on a characteristic time that does not grow, while the α-relaxation from the plateau takes place on a time scale that diverges when $T \to T_c$ (see fig. 1.2). This dynamic transition is exactly described by the schematic mode-coupling equations.

However, the existence of a dynamic relaxation at a temperature above the true thermodynamic one is possible only in mean-field, and the conjecture [13] is that, in a realistic system like a glass, the region between T_K and T_c will have instead a finite, but very rapidly increasing, relaxation time, as explained in fig. 1.2. A similar behavior has been found in finite-size, mean-field models [21].

Another very interesting dynamical regime is the one in which the system is out of equilibrium ($T < T_g$). The system is then no longer stationary: it ages. This is well known, for instance, from studies in polymeric glasses. If one measures the response of one's favorite plastic ruler to stress, it will behave differently depending on its age. Schematically, new relaxation processes come into play on a time scale comparable to the age of the system: the older the system, the longer the time needed for this "aging" relaxation to take place. Recent years have seen important developments in the out-of-equilibrium dynamics of the glassy phases [22], initiated by the exact solution of the dynamics in a discontinuous spin glass by Cugliandolo and Kurchan [23]. It has become clear that, in realistic systems with short-range interactions, the pattern of replica symmetry

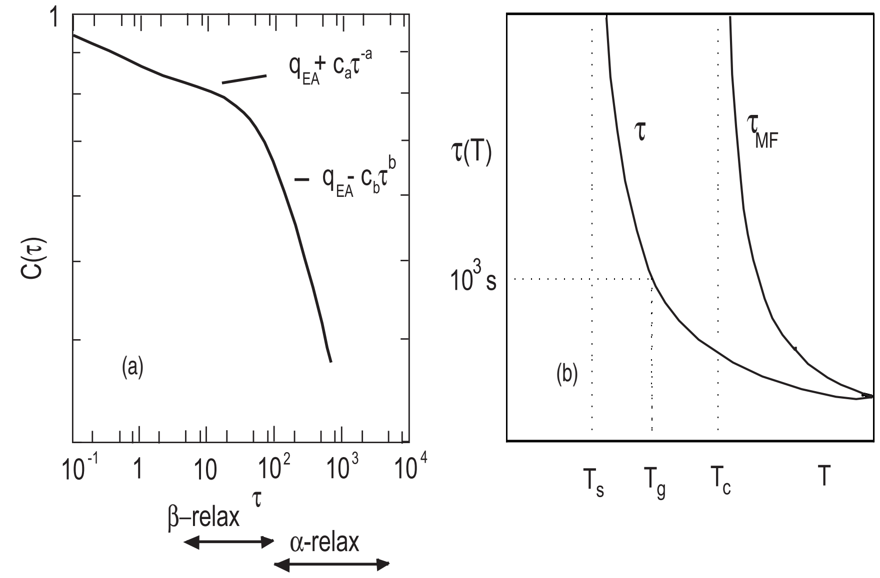

Figure 1.2: The left-hand figure (a) shows the schematic behavior of the correlation function found in mean-field discontinuous spin glasses and observed in structural glasses. The typical two-step relaxation consists of a fast β-relaxation leading to a plateau, followed by an α-relaxation from the plateau, whose typical time scale increases rapidly as T decreases, and diverges at $T = T_c$, which is equal to the mode-coupling transition temperature. The right-hand figure (b) shows the behavior of the relaxation time versus T. The right-hand curve is the prediction of mode-coupling theory without any activated processes: it is a mean-field prediction that is exact for instance in the discontinuous mean-field spin glasses [18]. The left-hand curve is the observed relaxation time in a glass. The mode-coupling theory provides a quantitative prediction for the increase of the relaxation time with decreasing T, at high temperatures (well above the mode coupling transition T_c) [19, 20]. The departure from the mean-field prediction at lower temperatures is usually attributed to 'hopping' or 'activated' processes, in which the system is trapped for a long time in a valley, but can eventually jump out of it. The ideal glass transition, which takes place at T_K, cannot be observed directly since the system falls out of equilibrium on laboratory time scales at the 'glass temperature' T_g.

breaking can be deduced from measurements of the violation of the fluctuation-dissipation theorem [24]. These measurements are difficult. However, numerical simulations performed on different types of glass-forming systems have provided an independent and spectacular confirmation of their 'one-step-RSB' structure [25, 26, 27, 28] on the (short) time scales that are accessible. Experimental results have not yet settled the issue, but the first measurements of effective temperatures in the fluctuation-dissipation relation was made recently [29].

To summarize, the analogy between the phenomenology of fragile glass formers and discontinuous mean-field spin glasses accounts for:

- The discontinuity of the order parameter
- The continuity of the energy and the entropy
- The jump in specific heat (and the sign of the jump)
- Kauzmann's "entropy crisis"
- The two-step relaxation of the dynamics, and the success of Mode-Coupling Theory at relatively high temperatures.
- The aging phenomenon and the pattern of modification of the fluctuation dissipation relation in the low-T phase

1.5 A LESSON FROM MEAN-FIELD: MANY VALLEYS

The successes of the above analogy suggest that we should have a closer look at the mean-field models to understand, at least at the mean-field level, the basic ingredients that are at work in the glass transition. In mean-field spin glasses, at temperatures $T_K < T < T_c$, the phase space breaks up into ergodic components that are well-separated, the so-called free-energy valleys or TAP states [30, 31]. Each valley α has a free energy F_α and a free-energy density $f_\alpha = F_\alpha/N$. The number of free-energy minima with free-energy density f is found to be exponentially large:

$$\mathcal{N}(f,T,N) \approx \exp(N\Sigma(f,T)), \tag{1.4}$$

where the function Σ is called the complexity. The total free energy of the system, Φ, may be well-approximated by:

$$e^{-\beta N\Phi} \simeq \sum_\alpha e^{-\beta N f_\alpha(T)} = \int_{f_{min}}^{f_{max}} df\ \exp\left(N[\Sigma(f,T) - \beta f]\right)\ , \tag{1.5}$$

where $\beta = 1/T$. The minima that dominate the sum are those with a free-energy density f^* that minimizes the quantity $\Phi(f) = f - T\Sigma(f,T)$. At large enough T, the saddle point is at $f > f_{min}(T)$. When one decreases T the saddle-point free-energy decreases (see Fig. 1.3, with $m = 1$). The Kauzman temperature T_K is that below which the saddle point sticks to the minimum: $f^* = f_{min}(T)$. It is a genuine phase transition [11, 12, 13]. However, because $T_c > T_K$, the phase space is actually separated into non-ergodic components (valleys) at $T < T_c$ (actually, some non-ergodic components also exist above T_c, but they are not accessed when the system starts from random initial conditions [32]). The total

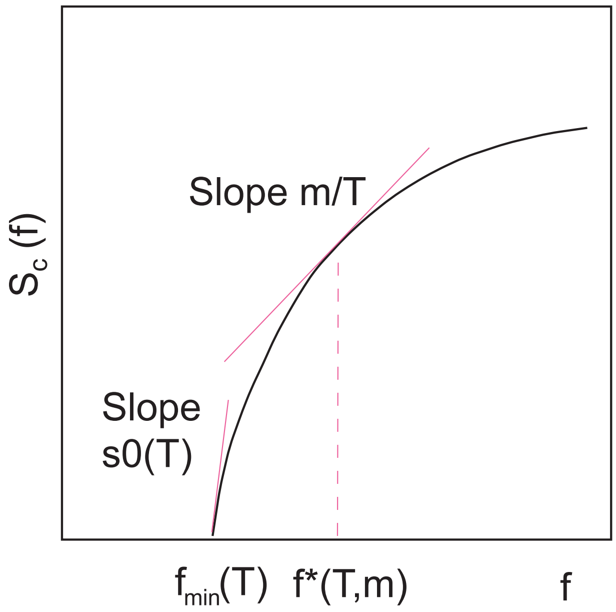

Figure 1.3: Qualitative shape of the complexity versus free energy in mean-field discontinuous spin glasses. The whole curve depends on the temperature. The saddle point that dominates the partition function, for m constrained replicas, is the point f^* such that the slope of the curve equals m/T (in the usual unreplicated system, $m = 1$). If $T$is small enough, the saddle point sticks to the minimum $f = f_{min}$, and the system is in its glass phase. For $m = 1$, this equilibrium phase transition occurs at $T = T_K$.

equilibrium free energy is analytic at T_c: in spite of the ergodicity breaking, the system has the same free energy as that of the liquid, as if transitions were allowed between valleys.

What remains of this mean-field picture in finite-dimensional glasses? When one decreases the temperature, there is a well-defined separation of time scales between the α and the β-relaxations. This suggests that we should regard the dynamical evolution of system in phase space as a superposition of two processes: an intravalley relaxation that is relatively fast, and an intervalley hopping process that is slow, and becoming dramatically slower with decreasing T.

A popular way of making this statement more precise (hence facilitating numerical studies) is to introduce 'inherent structures' (IS) [33]. Given a configuration of the system characterized by its phase space position $x = \{\vec{x}_1, ..., \vec{x}_N\}$, the corresponding inherent structure $s(x)$ is another point in phase space that is the local minimum of the Hamiltonian reached from the starting configuration via a steepest-descent dynamics. The inherent structures are readily identified numerically. A given trajectory $x(t)$ of the glass through phase space maps onto the corresponding trajectory $s(t)$ in the space of inherent structures. Looking at the dynamical evolution in the space of IS [34] makes the valley structure slightly more apparent, since one gets rid of the small thermal excitations around each valley minimum. Calling $\mathcal{D}_s$ the set of those configurations that are mapped into the coherent structure s, a natural definition of the IS entropy density Σ_{is} is $N\Sigma_{is}(T) = -\sum_s P(s)\ln(P(s))$, where the weight of the inherent structure s is

$$P(s) = Z(s)/\sum_b Z(b) \quad ; \quad Z(s) \equiv \int_{x\in\mathcal{D}_s} dx \exp(-\beta H(x)) \ . \tag{1.6}$$

In a system with short-range interactions, it is reasonable to expect that one may have two distinct IS that differ by a local rearrangement of a finite number of atoms. It is then easy to show that the slope of configurational entropy versus free energy is infinite around f_{min} [35], which does not agree with the general scenario, except when the Kauzmann temperature vanishes. This problem arises because the IS are objects that are too simple to be identified with the free energy valleys. The difference is very easily seen in spin systems [36]: IS are nothing but configurations that are stable against one spin flip. Zero-temperature free-energy valleys, defined as TAP states, are stable against the flip of an arbitrarily large number k of spins (but the limit $N \to \infty$ must be taken before the limit $k \to \infty$). In continuous systems, the generalization is clear: IS are local minima of the energy, so that any infinitesimal move of the positions of all N particles raises the energy. Let us generalize the notion of a minimum as follows: define a k-th order local minimum as a configuration of particles such that any infinitesimal move of all N particles, together with a move of *arbitrary size* of k particles, raises the energy. The limit $k \to \infty$ gives the proper definition of a zero-temperature, free-energy valley. The proper definition at finite T is slightly more involved [37]. Let us summarize it here briefly. Given two configurations x and y we define their overlap as before as $q(x,y) = -1/N\sum_{i,k=1,N} w(x_i - y_k)$, where $w(x) = -1 \quad \text{for} \quad x$ small, $w(x) = 0 \quad \text{for} \quad x$ larger than the typical interatomic distance. We add an extra term to the Hamiltonian: we define

$$\exp(-N\beta F(y,\epsilon)) = \int dx \exp(-H(x) + \beta\epsilon N q(x,y)), \qquad F(\epsilon) = \langle F(y,\epsilon)\rangle, \tag{1.7}$$

where $\langle f(y)\rangle$ denotes the average value of f over equilibrium configurations y thermalized at temperature β^{-1}. Taking the thermodynamic limit before the limit $\epsilon \to 0$ allows to identify the valley around any generic equilibrium configuration y [37, 39].

In a nutshell, two configurations that differ by the (arbitrarily large) displacement of a finite number of atoms are in the same thermodynamic valley. This definition of the valleys also suffers from some difficulties: Nucleation arguments then forbid the existence of a non-trivial complexity versus free energy curve in a finite-dimensional system. The solution consists in noticing that there exist many more metastable valleys that have a finite but very long lifetime. These can be identified by taking the Legendre transform $W(q)$ of the free energy $F(\epsilon)$:

$$W(q) = F(\epsilon) + \epsilon q \quad ; \quad q = \frac{-\partial F}{\partial \epsilon} \ . \tag{1.8}$$

Analytic computation in mean-field models [37], as well as in glass-forming liquids, using the replicated HNC approximation [38], show that $W(q)$ is minimal at $q = 0$, but has a secondary minimum at a certain $q = q_{EA}$, in the temperature range $T_K < T < T_c$. The behavior around this second, metastable, minimum corresponds to phenomena that can be observed on time scales shorter than the lifetime of the metastable state. The thermodynamic configurational entropy is the value of the potential $W(q)$ at the secondary minimum with $q \neq 0$ [37], and it can be defined only if the minimum exists (i.e. for $T < T_c$). Of course, the secondary minimum for $T > T_k$ is always in the metastable region. However, if one starts from a large value of ϵ and decreases ϵ to zero (not too slowly), the system should not escape from the metastable region. One then obtains a proper definition of the thermodynamic configurational entropy in this region $T > T_K$. In a similar way one may compute $q(\epsilon)$ in the region ($\epsilon > \epsilon_c$) where the high q phase is thermodynamically stable, and extrapolate it to $\epsilon \to 0$. The ambiguity in the definition of the thermodynamic configurational entropy at temperatures above T_k becomes larger and larger as T increases. It cannot be defined for $T > T_c$.

1.6 Beyond the analogy: first-principles computation

In recent years, it has become possible to go beyond the simple analogy between structural glasses and mean-field discontinuous spin glasses. One can actually use the concepts and the techniques that are suggested by this analogy to start a systematic, first-principles study of the glass phase [41, 42, 39]. So far, we have focused on the equilibrium study of the low-T phase. The reason is that the direct study of out-of-equilibrium dynamics is more difficult, and one might be able to make progress by a careful analysis of the landscape [40]. One assumes that there exists a phase transition, and that it is of the same type as observed in discontinuous mean-field spin glasses. Within this framework, one tries to compute the properties of the glass phase. This involves several quantitites like the Kauzmann temperature, the radius of the cage that confines the particles in the glass phase, the configurational entropy, and so on. The validity of the scenario is checked from the comparison of various predictions with numerical simulations of well-equilibrated systems.

The first task is to define an order parameter. This is not trivial in an equilibrium theory in which we have no notion of time-persistent correlations. The best way is to introduce two copies of the system, with a weak interaction. The two sets of particles have positions x_i and y_i, respectively, the total Hamiltonian is

$$E = \sum_{1 \le i \le j \le N} (v(x_i - x_j) + v(y_i - y_j)) + \epsilon \sum_{i,j} w(x_i - y_j) \tag{1.9}$$

where we have introduced a small attractive potential $w(r)$ between the two systems. The precise shape of w is irrelevant, insofar as we shall be interested in the limit $\epsilon \to 0$, but its range should be of order or smaller than the typical interparticle distance. The order parameter is then the correlation function between the two systems:

$$g_{xy}(r) = \lim_{\epsilon \to 0} \lim_{N \to \infty} \frac{1}{\rho N} \sum_{ij} < \delta(x_i - y_j - r) > . \tag{1.10}$$

In the liquid phase this correlation function is identically equal to one, while it has a nontrivial structure in the glass phase, reminiscent of the pair-correlation in a dense liquid, but with an extra peak around $r \simeq 0$. Let us notice that we expect a discontinuous jump of this order parameter at the transition, despite its second-order nature (in the thermodynamic sense). The existence of a non-trivial order parameter is associated with the spontaneous breaking of a symmetry: For $\epsilon = 0$, with periodic boundary conditions, the system is symmetric under a global translation of the x particles with respect to the y particles. This symmetry is spontaneously broken in the low-T phase, where the particles of each subsystem tend to sit in front of each other.

Generalizing this approach to a system of m coupled replicas, sometimes named 'clones' in this context (the order parameter used only $m = 2$), provides a wonderful method for studying analytically the thermodynamics of the glass phase [43, 44]. In the glass phase, the attraction will force all m systems to fall into the same glass state, so that the partition function is:

$$Z_m = \sum_\alpha e^{-\beta N m f_\alpha(T)} = \int_{f_{min}}^{f_{max}} df \ \exp\left(N[\Sigma(f,T) - m\beta f]\right). \tag{1.11}$$

In the limit $m \to 1$ the corresponding partition function Z_m is dominated by the correct saddle point f^* for $T > T_K$. The interesting regime is when $T < T_K$, and the number m is allowed to become smaller than one. The saddle point $f^*(m,T)$ in the expression (1.11) is the solution of $\partial\Sigma(f,T)/\partial f = m/T$. Because of the convexity of Σ as function of f, the saddle point is at $f > f_{min}(T)$ when m is small enough, and it sticks at $f^* = f_{min}(T)$ when m exceeds a certain value $m = m^*(T)$, which is smaller than one if $T < T_K$ (see fig. 1.3). The free energy in the glass phase, $F(m = 1, T)$, is equal to $F(m^*(T), T)$. As the free energy is continuous along the transition line $m = m^*(T)$, one can compute $F(m^*(T), T)$ from the region $m \le m^*(T)$, where the replicated system is in the liquid phase. This is the clue to the explicit computation of the free energy in the glass phase. It may sound a bit strange because one is tempted to think of m as an integer number. However, the computation is much clearer if one regards m as a real parameter in (1.11). As one considers low temperatures $T < T_K$ the m coupled replicas fall into the same glass state. Hence, they assemble some molecules of m atoms, each molecule being built from one atom of each 'color'. Now, the strength of the interaction between the molecules is basically rescaled by a factor m (this statement becomes exact in the limit of zero temperature where the molecules are point-like). If m is small enough, this interaction is small, and the system of molecules is a liquid. When m increases, the molecular fluid freezes into a glass state at the value $m = m^*(T)$. Thus, the method requires us to estimate the replicated free energy, $F(m,T) = -\log(Z_m)/(\beta m N)$, in a molecular liquid phase, where the molecules consist of m atoms, with m smaller than one. For $T < T_K$, $F(m,T)$ is maximum at a value $m = m^*$ smaller than one, whereas for $T > T_K$, the maximum is reached at a value m^* larger than one. The knowledge of F_m as a function of m allows us to reconstruct the configurational entropy function $Sc(f)$ at a given T via a Legendre transform, using the parametric representation

$$f = \frac{\partial \left[mF(m,T)\right]}{\partial m} \quad ; \quad \Sigma(f) = \frac{m^2}{T}\frac{\partial F(m,T)}{\partial m} \; . \tag{1.12}$$

(This is easily deduced from a saddle-point evaluation of Eq. 1.11 [43].) The Kauzmann temperature ('ideal glass-temperature') is that at which $m^*(T_K) = 1$. For $T < T_K$ the equilibrium configurational entropy vanishes. Above T_K one obtains the equilibrium configurational entropy $\Sigma(T)$ by solving Eq. 1.12 at $m = 1$.

This gives the main idea that enables the free energy in the glass phase for $T < T_K$ to be computed from first principles. It is equal to the free energy of a molecular liquid at the same T, in which each molecule is built of m atoms, and an appropriate analytic continuation to $m = m^*(T) < 1$ has been taken. The whole problem is reduced to a computation in a liquid. This is not a trivial task, and requires specific approximations to be adopted. I refer the reader to the original papers [42, 45, 46, 47]. The basic idea of the approximation is that the size of the molecules is directly related to the thermal wandering of an atom in its cage. Therefore, at low temperatures one can use some small-cage approximation. It is natural to write the partition function in terms of the center-of-mass and relative coordinates $\{r_i, u_i^a\}$, with $x_i^a = r_i + u_i^a$ and $\sum_a u_i^a = 0$, and to expand the interaction in powers of the relative displacements u. Keeping only the term quadratic in u (harmonic vibrations of the molecules), and integrating over these vibration modes, one gets the 'harmonic resummation' approximation in which the partition function is given by:

$$Z_m = Z_m^0 \int dr \exp\left(-\beta m H(r) - \frac{m-1}{2} Tr \log M\right) , \tag{1.13}$$

where $Z_m^0 = m^{Nd/2}\sqrt{2\pi T}^{Nd(m-1)}/N!$, and the matrix M, of dimension $dN \times dN$, is given by

$$M_{(i\mu)(j\nu)} = \frac{\partial^2 H(r)}{\partial r_i^\mu \partial r_j^\nu} = \delta_{ij} \sum_k v_{\mu\nu}(r_i - r_k) - v_{\mu\nu}(r_i - r_j), \tag{1.14}$$

and $v_{\mu\nu}(r) = \partial^2 v / \partial r_\mu \partial r_\nu$ (the indices μ and ν denote space directions). Now we are back to a real problem of liquid theory, since we have only d degrees of freedom per molecule (the center of mass coordinates), and the number of clones, m, appears as a parameter in (1.13).

Once one has derived an expression for the replicated free energy, one can deduce from it the whole thermodynamics, as described above (notice that the 'technical' approximation of neglecting the exchange of atoms between different molecules, as well as using a harmonic model, means that one really studies the IS in this computation, rather than the real free energy valleys). In all three cases, one finds an estimate of the Kauzmann temperature that is in reasonable agreement with simulations, with a jump in specific heat, from a liquid value at $T > T_K$ to the Dulong-Petit value C = 3/2 below T_K (we have included only positional degrees of freedom). This is similar to the experimental result, where the glass specific-heat jumps down to the crystal value as T decreases (our approximations so far are similar to the Einstein approximation of independent vibrations of atoms, in which case the contribution of positional degrees of freedom to the crystal specific heat is C = 3/2). The parameter $m^*(T)$ and the cage sizes are nearly linear in T in the whole glass phase. This means, in particular, that the effective temperature T/m is always close to T_K, so in our theoretical computation we need only to evaluate the expectation values of observables in the liquid phase at temperatures where the HNC approximation for the liquid still works quite well.

A more detailed numerical check of these analytical predictions involves the measurement of the complexity,

$$\Sigma_t = S(T) - S_{valley}(T). \tag{1.15}$$

The liquid entropy is estimated by a thermodynamic integration of the specific heat from the very dilute (ideal gas) limit. It turns out that in the deeply supercooled region the T dependence of the liquid entropy is well-fitted by the law predicted in [48]: $S_{liq}(T) = aT^{-2/5} + b$, which presumably allows for a good extrapolation at temperatures that cannot be simulated. As for the 'valley' entropy, it may be estimated as that of an harmonic solid. One needs, however, the vibration frequencies of the solid. These have been approximated by several methods, most of which are based on some evaluation of the Instantaneous Normal Modes (INM) [50] in the liquid phase, and the assumption that the spectrum of frequencies does not depend much on T below T_K.

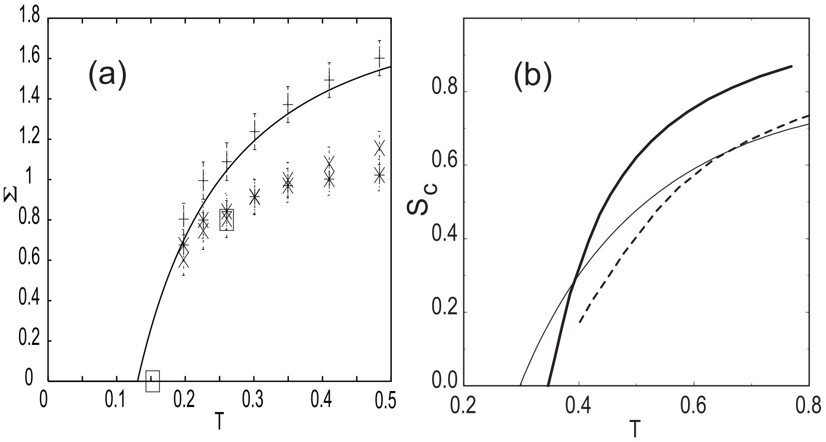

Figure 1.4: The configurational entropy versus T in binary mixtures of soft spheres (Panel (a)) and of Lennard-Jones particles (b). The soft-sphere result (a), from [45], compares the analytical prediction obtained within the harmonic resummation scheme (full line), to simulation estimates of $S_{liq} - S_{valley}$, where the valley entropy is that of a harmonic solid with INM eigenvalues projected onto positive eigenvalues (+), taken in absolute values ($\times$), or taken around the nearest inherent structure ($*$). The squares correspond to the numerical estimate of the thermodynamic configurational entropy obtained by studying the system coupled to a reference configuration (see text, and Ref. [45] for details). In the Lennard-Jones system (b), the prediction obtained from the cloned molecular liquid approach [46, 47] is displayed as a thick, solid line. The broken line is the result from the simulations in Ref. [46, 47], while the thin, solid line is from simulations in Ref. [51]. Both simulations use the $S_{liq} - S_{valley}$ estimate in which the harmonic solid vibration modes are approximated by the ones of the nearest inherent structure.

Starting from a typical configuration of the liquid, one can look at the INM around it. In general, there exist some negative eigenvalues (the liquid is not a local minimum of the energy) that one must take care of. Several methods have been tried: either one keeps only the positive eigenvalues, or one considers the absolute values of the eigenvalues [45, 46, 47]. Alternatively, one may also consider the INM around the nearest inherent structure that has, by definition, a positive spectrum [45, 46, 47, 51]. This procedure really measures the configurational entropy rather than the thermodynamic complexity. The computation of the thermodynamic complexity, using its definition as a system coupled to a reference thermalized configuration, has also been computed in Ref. [45], and turns out to be not very different from the configurational entropy, on the time and temperature scales that have been studied so far (they must differ on infinitely long time scales, as we discussed in the previous section).

The results for the configurational entropy as a function of T are shown in

Fig. 1.4, for binary mixtures of soft spheres and of Lennard-Jones particles. The agreement with the analytical result obtained from the replicated fluid system is rather satisfactory, considering the approximations in both analytical and numerical approaches.

1.7 CONCLUSION

Our knowledge of first-principle computations of glasses is still rather primitive. Basically, we have obtained for the glass the equivalent of the Einstein approximation for the crystal. Even within this simple scheme, doing the actual computation for the glass turns out to be rather formidable. For further progress, we need: on the analytical side, better approximations of the molecular liquid state that allow us to go beyond the small cage expansions, and reliable estimate of time scales in the regime $T_K < T < T_c$; on the numerical side, some precise results in the glass phase at equilibrium [52]. On the experimental side, we need more measurements of the fluctuation-dissipation ratio in the out-of-equilibrium dynamics. No doubt, "... there are still fascinating questions of principle about glasses and other amorphous phases..." [2].

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