

## Thermodynamics of Glasses: A First Principles Computation

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We propose a first principles computation of the equilibrium thermodynamics of simple fragile glasses starting from the two body interatomic potential. A replica formulation translates this problem into that of a gas of interacting molecules, each molecule being built of  $m$  atoms, and having a gyration radius (related to the cage size) which vanishes at zero temperature. We use a small cage expansion, valid at low temperatures, which allows us to compute the cage size, the specific heat (which follows the Dulong and Petit law), and the configurational entropy. [S0031-9007(98)08247-7]

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Take a three-dimensional classical system consisting of  $N$  particles, interacting by pairs through a short range potential  $v(r)$ . Very often this system will undergo, upon cooling or upon density increasing, a solidification into an amorphous solid state—the glass state. The condition required for observing this glass phase is the avoidance of crystallization, which can always be obtained either through a fast enough quench (the meaning of “fast” depends very much on the type of system) [1] or by using appropriately frustrated binary mixtures of hard spheres, soft spheres, or Lennard-Jones particles, as seen in recent simulations [2–6].

Our aim is to compute the thermodynamic properties of this glass phase, starting from the microscopic Hamiltonian. The general framework of our approach finds its roots in the old ideas of [7,8], which have also been studied in some generalized mean field spin glasses, opening the way to a fruitful analogy between the two fields [9]. In this framework, which should provide a good description of fragile glass formers, the glass transition, measured from dynamical effects, is associated with an underlying thermodynamic transition at the Kauzmann or Vogel-Fulcher temperature  $T_K$  [1]. This transition is of an unusual type, since it presents two apparently contradictory features: (i) The order parameter, defined as the inverse radius of the cage seen by each particle, jumps discontinuously from 0 in the liquid phase to a finite value in the glass phase. (ii) The transition is continuous (second order) from the thermodynamical point of view, with a continuous free energy and a jump in the specific heat. These properties are indeed observed in generalized spin glasses [9,10], although these have quenched disorder which is absent in structural glasses. The recent discovery of some generalized spin glass systems without quenched disorder [11] strongly suggests that this similarity is not fortuitous.

In order to turn this general idea into a consistent computational scheme, a first important step, which we shall review below, was the idea of using several copies of the same system in order to characterize the glass

phase [12,13]. The next step, which we carry here, is to understand and compute the correlations between the copies and translate them into the physical properties of the glass phase. In a previous preliminary study, we used some of these ideas to estimate the glass temperature, arriving from the liquid phase, but we could not study the glass phase itself, because we did not take into account the formation of bound states between these copies [14]. The treatment of the bound states which we develop here, using new methods, is the key to the analytic study of the glass phase.

The main obstacle to a study of the glass phase is the very description of the amorphous solid state. A simple idea, originally developed in the spin glass context [15,16], is to consider two copies (sometimes called “replicas”) of the system, with an infinitesimal extensive attraction. The low temperature phase is identified from the fact that the two replicas remain close to each other in the limit of vanishing coupling.

This method can be generalized to study glasses, but one must be careful to take into account the degeneracy of glass states. This property can be studied in detail in generalized spin glass mean field models [17,18]. For structural glasses, this is a conjecture which we shall make, on the basis of its agreement with the phenomenology of glasses [6,9]. Let us introduce a free energy functional  $F(\rho)$  which depends on the density  $\rho(x)$  and on the temperature. We suppose that at sufficiently low temperature this functional has many minima (i.e., the number of minima goes to infinity with the number  $N$  of particles). Exactly at zero temperature these minima, labeled by an index  $\alpha$ , coincide with the minima of the potential energy as function of the coordinates of the particles. To each of them we can associate a free energy  $F_\alpha$  and a free energy density  $f_\alpha = F_\alpha/N$ . The number of free energy minima with free energy density  $f$  is supposed to be exponentially large:

$$\mathcal{N}(f, T, N) \approx \exp[N\Sigma(f, T)], \quad (1)$$

where the function  $\Sigma$  is called the complexity or the configurational entropy (it is the contribution to the entropy coming from the existence of an exponentially large number of locally stable configurations). This function is not defined in the regions  $f > f_{\max}(T)$  or  $f < f_{\min}(T)$ , where  $\mathcal{N}(f, T, N) = 0$ ; it is concave and it is supposed to go to zero at  $f_{\min}(T)$ , as found in all existing models so far. In the low temperature region the total free energy of the system ( $f_S$ ) can be well approximated by

$$e^{-\beta N f_S} \simeq \sum_a e^{-\beta N f_a} = \int_{f_{\min}}^{f_{\max}} df e^{-N[\beta f - \Sigma(f, T)]}. \quad (2)$$

The minima which dominate the sum are those with a free energy density  $f^*$  which minimizes the quantity  $f - \Sigma(f, T)/\beta$ . The Kauzmann temperature  $T_K$  is that below which the saddle point sticks at the minimum:  $f^* = f_{\min}(T)$ .

In order to cope with this degeneracy of states, it is useful to introduce  $m$  replicas of the problem, coupled through a small extensive attraction which will eventually go to zero [13]. In the glass phase, the attraction will force all  $m$  systems to fall into the same glass state, so that the partition function is

$$Z_m = \int_{f_{\min}}^{f_{\max}} df e^{-N[m\beta f - \Sigma(f, T)]}. \quad (3)$$

In the limit where  $m \rightarrow 1$  the corresponding partition function  $Z_m$  is dominated by the correct saddle point  $f^*$  for  $T > T_K$ . When the temperature is  $T < T_K$ , the saddle point  $f^*$  sticks at  $f^* = f_{\min}(T)$ , and the replicated free energy  $F_m = -\log(Z_m)/\beta m$  is maximum at a value of  $m = m^*$  smaller than one. One can use expressions valid in the liquid phase (i.e., high temperature formulas) to evaluate the free energy  $F_m$  at  $m < m^*$ . Notice that the replicas which we introduce here play a slightly different role compared to the ones used in disordered systems: there is no quenched disorder here and no need to average a logarithm of the partition function. Replicas are introduced to define the amorphous state in the framework of equilibrium statistical mechanics. There is no “zero replica” limit, but there is, as in disordered systems, an analytic continuation in the number of replicas. We shall see that this continuation looks rather innocuous. An alternative and complementary method is to introduce a real coupling of the system to another system which is thermalized [5,12,19].

Let us turn to a more explicit implementation of these ideas. The original partition function is

$$Z = \frac{1}{N!} \int \prod_{i=1}^N dx_i \exp\left(-\beta \sum_{1 \leq i < j \leq N} v(x_i - x_j)\right), \quad (4)$$

where the  $N$  indistinguishable particles move in a volume  $V$  of a  $d$ -dimensional space, and we shall take the thermodynamic limit  $N, V \rightarrow \infty$  at fixed density  $\rho = N/V$ . For simplicity, we do not consider here the description of

mixtures, which is presumably an easy generalization. We introduce  $m$  replicas of each particle, with positions  $x_i^a$ ,  $a \in 1, \dots, m$ , and compute  $Z_m$  in the presence of an infinitesimal pinning field which is an attractive potential  $w$  between them. This attractive potential must be of short range (the range should be less than the typical interparticle distance in the solid phase), and must not break the indistinguishability of all  $N$  particles with the same replica index, but its precise form is irrelevant.

A large attraction gives rise to the formation of *molecular bound states* of  $m$  atoms. The appearance of the glass states ( $T \leq T_D$ ) is signaled by the fact that these molecules still exist in the limit  $\lim_{m \rightarrow 1} \lim_{w \rightarrow 0} \lim_{N \rightarrow \infty}$  (notice the order of limits). According to the above discussion, the ideal glass transition ( $T_K$ ) is detected from the existence, at  $T < T_K$ , of a maximum of the replicated free energy  $F_m = -\log(Z_m)/\beta m$  at a value of  $m$  less than 1. This is a well defined mathematical problem, which fully describes our general strategy for computing the thermodynamics of the glass state. Of course this cannot be done without resorting to some approximation schemes. We shall now develop one of them, a kind of harmonic expansion in the solid phase, but several other approximation schemes can be developed [20].

We are interested in the regime of low temperatures where the molecules have a small radius, justifying a quadratic expansion of  $v$  [we work here with a regular potential  $v(r)$ , excluding hard cores]. We thus write the partition function in terms of the center of mass and internal variables  $z_i, u_i^a$ , with  $x_i^a = z_i + u_i^a$  and  $\sum_a u_i^a = 0$ , expand the energy to second order in  $u$ , and integrate over these quadratic fluctuations, leading to

$$Z_m = Z_m^0 \int \prod_{i=1}^N dz_i e^{-\beta m \sum_{i < j} v(z_i - z_j) - [(m-1)/2] \text{Tr} \log M}, \quad (5)$$

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

$$M_{(i\mu)(j\nu)} = \beta \delta_{ij} \sum_k v_{\mu\nu}(z_i - z_k) - \beta v_{\mu\nu}(z_i - z_j) \quad (6)$$

and  $v_{\mu\nu}(r) = \partial^2 v / \partial r_\mu \partial r_\nu$  (the indices  $\mu$  and  $\nu$ , running from 1 to  $d$ , denote space directions). We have thus found an effective Hamiltonian for the centers of masses  $z_i$  of the molecules, which basically looks like the original problem at the effective temperature  $T^* = 1/\beta m$ , complicated by the contribution of vibration modes. We shall proceed by using a “quenched approximation,” i.e., neglecting the feedback of vibration modes onto the centers of masses, which amounts to substituting  $\langle \exp(-\frac{m-1}{2} \text{Tr} \log M) \rangle$  by  $\exp(-\frac{m-1}{2} \langle \text{Tr} \log M \rangle)$ , where  $\langle \cdot \rangle$  is the Boltzmann expectation value at the effective temperature  $T^*$ .

Computing the spectrum of  $M$  is an interesting problem of random matrix theory, in a subtle case where the matrix

elements are correlated. Some efforts have been devoted to such computations in the liquid phase where the eigenmodes are called instantaneous normal modes [21]. It might be possible to extend these approaches to our case. Here we shall rather propose a simple resummation scheme which should be reasonable at high densities/low temperatures and which also enforces automatically the positivity of the spectrum (which is guaranteed in the original “annealed” case for  $m < 1$  but not automatic in the quenched approximation). Considering first the diagonal elements of  $M$ , we notice that in this high density regime there are many neighbors to each point, and thus a good approximation is to neglect the fluctuations of these diagonal terms and substitute them by their average value,  $r_0 \equiv \frac{\beta}{d} \int dr g(r) \nabla^2 v(r)$ , with  $g(r)$  the pair correlation in the liquid at the effective temperature  $T^*$ . Expanding  $\langle \text{Tr} \log(M/r_0) \rangle$  in powers of  $1/r_0$ , the  $p$ th order term is

$$\begin{aligned} M_p \equiv & \int dx_1, \dots, dx_p g(x_1, \dots, x_p) \\ & \times v_{\mu_1 \mu_2}(x_1 - x_2), \dots, v_{\mu_{p-1} \mu_p}(x_{p-1} - x_p) \\ & \times v_{\mu_p \mu_1}(x_p - x_1), \end{aligned} \quad (7)$$

which involves the  $p$  points correlation function of the liquid at the effective temperature  $T^*$ . Observing that  $v_{\mu\nu}(r)$  is a function which is very peaked at short

distance, we see that the most important effect of the multiple correlation function is its vanishing when two points get near one to the other. We have thus used a “chain” approximation involving only the product of pair correlations, which consists of writing

$$M_p \approx \int \frac{dk}{(2\pi)^d} [a_{\parallel}(k)^p + (d-1)a_{\perp}(k)^p], \quad (8)$$

where  $a_{\parallel} = a + \frac{d-1}{d}b$  and  $a_{\perp} = a - \frac{1}{d}b$ , and the functions  $a$  and  $b$  are the Fourier transforms of  $v_{\mu\nu}$ :

$$\begin{aligned} \int dr g(r) v_{\mu\nu}(r) e^{ikr} & \equiv \delta_{\mu\nu} a(k) \\ & + \left( \frac{k_{\mu} k_{\nu}}{k^2} - \frac{\delta_{\mu\nu}}{d} \right) b(k). \end{aligned} \quad (9)$$

This chain approximation selects those contributions which survive in the high density limit; systematic corrections could probably be computed in the framework of the approach of [22]; we leave this for future work. Here and in what follows, we have not written explicitly the density: we choose to work with density unity and vary the temperature (density and temperature variations are directly related in soft sphere systems onto which we focus below).

The free energy within the chain approximation is

$$\begin{aligned} \frac{\beta F_m}{N} = & -\frac{d \log m}{2m} - \frac{\log Z(T^*)}{mN} + \frac{d(m-1)}{2m} \log \left( \frac{\beta r_0}{2\pi} \right) \\ & + \frac{(m-1)}{2m} \int \frac{dk}{(2\pi)^d} \left[ L_3 \left( \frac{a_{\parallel}(k)}{r_0} \right) + (d-1)L_3 \left( \frac{a_{\perp}(k)}{r_0} \right) \right] - \frac{(m-1)}{4m} \int dr g(r) \sum_{\mu\nu} \frac{v_{\mu\nu}(r)^2}{r_0^2}, \end{aligned} \quad (10)$$

where the function  $L_3$  is defined as

$$L_3(x) = \log(1-x) + x + x^2/2. \quad (11)$$

We can thus compute the replicated free energy  $f_m$  solely from the knowledge of the free energy and the pair correlation of the liquid at the effective temperature  $T^*$ . We have done this computation in the case of soft spheres in three dimensions with  $v(r) = 1/r^{12}$ , using the free energy and pair correlation function of the liquid given by the hypernetted chain approximation [obviously one could try to use better schemes of approximation for the liquid, depending on the form of  $v(r)$ , in order to improve the results; our point here is not to try to get the most precise results but to show the feasibility of a quantitative computation of glass properties using the simplest approximations]. We find (always at density unity) a Kauzmann temperature  $T_K \approx 0.194$ . When converted into the usual dimensionless parameter  $\Gamma = \rho T^{-1/4}$ , this gives  $\Gamma_K \approx 1.51$  which is close to the glass temperature ( $\Gamma \sim 1.6$ ) observed in simulations [23] with very fast cooling to avoid crystallization. Simulations done on binary mixtures (which do not crystallize) give a similar value for  $\Gamma$ .

In Fig. 1 we show the results for the various properties of the glass phase. The effective temperature  $T^*$  varies

very little in the whole glass phase and remains close to the Kauzmann temperature. The square cage radius  $A$ , defined as  $A = \frac{1}{3}(\langle x_i^2 \rangle - \langle x_i \rangle^2)$ , is nearly linear in temperature in the whole glass phase, which is natural since nonharmonic effects have been neglected. The value of  $A$  at the Kauzmann temperature is  $A \sim 2.5 \times 10^{-3}$ . This corresponds to a typical lateral displacement of the particle in each direction of order  $\sqrt{A} \sim 0.05$ , which is 0.045 of the mean interparticle distance, a value which gives the correct order of magnitude for the Lindeman ratio. The specific heat closely follows the Dulong-Petit law. This is the result that one should obtain since we study a solid phase in the classical framework. Notice that it is not at all trivial to derive this law from first principles in the glass phase. It is interesting to see it coming out naturally from our computations: although we are basically using the properties of the liquid at the effective temperature  $T^*$ , the fact that the optimal number of replicas  $m$  vanishes linearly with  $T$  at low temperatures naturally gives the Dulong-Petit law.

From the knowledge of  $F_m$  as a function of  $m$ , we can compute the configurational entropy as a function of the free energy. In Fig. 2 we plot the result for  $\Sigma(f)$  versus  $f$  at three different temperatures. We see that the curves are

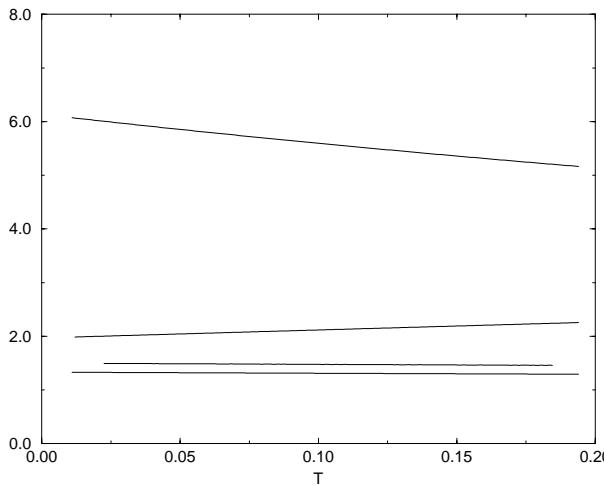


FIG. 1. The various parameters characterizing the glass phase, as a function of the temperature (the Kauzmann temperature is  $T_K \approx 0.194$ ). From top to bottom: the inverse effective temperature  $1/T^* = \beta m$  of the reference liquid, the internal energy, the specific heat, and the quantity  $100A/T$ , where  $A$  is the square cage radius (see text).

similar to each other, the main effect of the temperature changes being a shift in the  $f$  axis. As these temperatures all lie below  $T_K$ , the Boltzmann measure is dominated by states with zero configurational entropy.  $\Sigma(f)$  can also be computed above  $T_K$ ; this will be presented in a more expanded publication [20].

To summarize, we have developed a method for the analytic study of the thermodynamics of the glass phase. The basic knowledge one needs is the detailed properties of the liquid (particularly the instantaneous normal modes) close to the glass transition. We have shown that an implementation of this scheme with rather simple approximations leads to very reasonable results. We hope to be able to refine these approximations in the near future in order to get

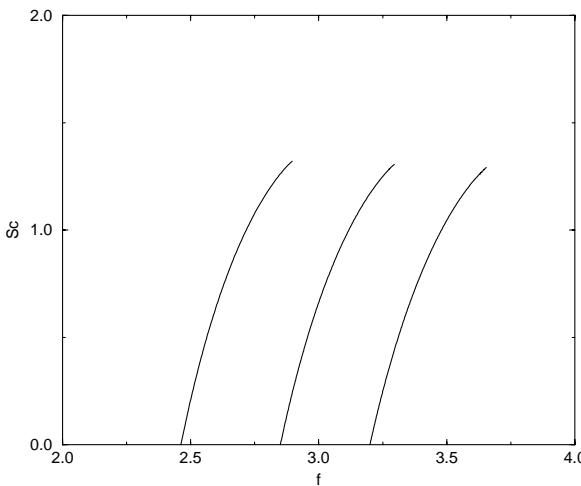


FIG. 2. The configurational entropy  $\Sigma(f)$  versus the free energy, at temperatures  $T = 0.05, 0.1, 0.15$  (from left to right).

very precise predictions. The extension of this approach to dynamical properties is also a fascinating perspective.

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