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# Thermodynamics and aging in supercooled liquids: the energy landscape approach

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## Abstract

We summarize some of the relevant information obtained from the study of the potential energy surface in the multidimensional configurational space sampled by a model supercooled liquid. Using the energy landscape approach we study both the equilibrium and the aging regimes of a prototypical binary Lennard–Jones liquid and, in both cases, we evaluate the relevant temperatures which characterize the system. From the theoretical point of view we introduce an expression for the free energy of the system which we show to be valid both in equilibrium and quasi-equilibrium aging situations. © 2002 Published by Elsevier Science B.V.

*Keywords:* Glass; Supercooling; Landscape

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## 1. Introduction

In the last decades there has been a renewed interest in the problems related to the physics of glasses, the structure and dynamics of which remain one of the most important unsolved problems of statistical physics [1]. Two apparently different approaches have been used to study glasses, namely the dynamical approach of mode-coupling theory (MCT) [2] and the equilibrium methods of spin-glass theory (SGT) [3]. MCT deals with structural glasses in the supercooled liquid regime and suggests the existence of a kinetic anomaly which gives rise to glass transition singularities of various orders. It is capable of giving many quantitative answers to various aspects of the behavior of supercooled liquids, with particularly good results when applied to colloidal systems. SGT works with idealized lattice spin models and has the merit of identifying the

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elementary mechanisms which are at the basis of the glass transition. The two approaches have been shown to be consistent in some particular case, e.g. the p-spin model which shares many of the qualitative features of the structural glasses [4]. More recently, a third approach is becoming widely used, the so-called energy landscape theory, which is particularly suitable for molecular dynamics, and which gives a transparent interpretation of the time scales which determine the short and long time behavior of a structural glass. In this paper we will summarize some of the results we have recently obtained using the energy landscape method.

## 2. The relevant temperatures in the glass transition

The behavior of a supercooled liquid is best characterised by a set of temperatures which were introduced in order to describe phenomenologically the features of a glass transition. The traditional way of defining the glass transition temperature  $T_g$  is by considering a typical thermodynamic quantity when lowering the temperature  $T$  with a constant cooling rate  $\gamma$ . Take for example the behavior at constant pressure of the volume  $V$  of a simple liquid as a function of  $T$  for given  $\gamma$ . If the latter is large enough the liquid is capable of avoiding crystallization at the melting temperature  $T_m$  and becomes supercooled. On further lowering  $T$  the smooth variation of  $V$  suddenly slows down signalling the formation of an amorphous solid, the glass, at  $T_g$ . Thus, since  $T_g$  depends on the cooling rate, it is clear that this temperature has no deep fundamental meaning, since it is just related to the time scale of the experiment.

There is a similar way of operationally defining  $T_g$  through dynamical quantities like a characteristic relaxation time or the shear viscosity  $\eta$ . One defines  $T_g$  as the temperature where  $\eta \approx 10^{12}$  Pa s. Two limiting behaviors are observed, on plotting  $\eta$  as a function of  $1/T$ , as originally suggested by Angell (for a review see, for example Ref. [5]),

- (i) the one followed by the so-called strong glasses, such as silica ( $\text{SiO}_2$ ), which closely follow an Arrhenius-like law;
- (ii) the fragile glass behavior, typically shown by OTP (ortho-ter-phenil), where a Vogel–Fulcher–Tammann (VFT) [6] law is typically observed

$$\eta(T) \sim \exp \left[ -\frac{E}{T - T_0} \right] \quad (1)$$

and  $E$  and  $T_0$  are material-dependent quantities.

A recent interesting observation relates an old attempt to explain the glass transition in terms of connected spatial regions, due to Adams and Gibbs [7], to the VFT law through the use of the configurational entropy  $S_c$ , a quantity we will introduce in what follows, since it plays a central role in the energy landscape approach. The previous authors made the hypothesis that the self-diffusion coefficient, or equivalently the inverse shear viscosity, should behave as

$$\eta^{-1}(T) \sim \exp \left[ -\frac{A}{TS_c} \right], \quad (2)$$

where  $A$  is approximately a constant. If one assumes a simple linear dependence on temperature of the product  $TS_c \sim T - T_0$ , the VFT law is obtained. The validity of Eq. (2) is currently under active investigation [8,9]. The so-called entropy crisis is the phenomenon which gave rise to the necessity of introducing another relevant quantity, the Kauzmann temperature  $T_K$  [10]. Experimentally the difference  $\Delta S = S_{liquid} - S_{crystal}$  between the liquid  $S_{liquid}$  and the crystal  $S_{crystal}$  entropy tends to diminish as we lower the temperature of a supercooled liquid. A simple extrapolation of the  $\Delta S$  vs.  $T$  curve would lead to the vanishing of the entropy difference at a finite temperature  $T_K$ . Before this actually happens, the glass transition sets in and the system avoids the entropy crisis. The Kauzmann temperature has been often related to the still open question of the possible existence of an underlying singularity related to a *thermodynamic* glass transition. The study of the behavior of a supercooled liquid in the vicinity of  $T_K$  would give important information on the transition.

The mode-coupling temperature  $T_{MCT}$  was introduced in the context of the corresponding theory of the glass transition in supercooled liquids due mainly to Götze and collaborators [2]. The theory predicts the possibility of a non-ergodicity transition of dynamical origin related to the long-time behavior of the density time correlation function. The MCT characterises also the separation of the time scales in the density correlator, clearly separating the short time dynamics from the regions of approach to the ergodicity breaking and the final extremely slow relaxation. In real fluids when the system is close enough to  $T_{MCT}$  the so-called hopping mechanisms set in and the liquid avoids the complete structural arrest. The theory has been tested with great success in a variety of systems [11], including in particular colloidal systems, where  $T_{MCT}$  appears to be very close to  $T_K$ . Essentially the behavior of supercooled liquids for moderately low temperatures is well described by MCT, and the melting temperature  $T_m$  and  $T_{MCT}$  delimit this region.

In conclusion the behavior of a supercooled liquid below melting can be characterised by the following set of temperatures  $T_K < T_g < T_{MCT} < T_m$  which in some cases are defined only in a limiting sense, but give a good starting point for the definition of the various dynamical regimes of supercooled liquid, as we will show in the next sections.

### 3. The energy landscape and the inherent structures

The potential energy  $\Phi(\{\mathbf{r}^N\})$  of a system of  $N$  classical particles as a function of their coordinates is a hypersurface in a  $(3N + 1)$ -dimensional space, the energy landscape. It was introduced many years ago by Goldstein [12] and extensively used by Stillinger and Weber [13,14]. Only more recently, with the advent of large computing facilities, it has become feasible to study numerically the structure of the energy landscape and to derive important information on dynamics of supercooled liquids. The potential energy surface (PES) of supercooled liquids is expected to contain a large number of local minima, named inherent structures (IS). Each minimum is surrounded by a basin which is the set of all configurations that, using a local minimization of the potential energy, will end up in that particular IS. The configuration space can be uniquely partitioned into a sum of basins, among which one expects to find the

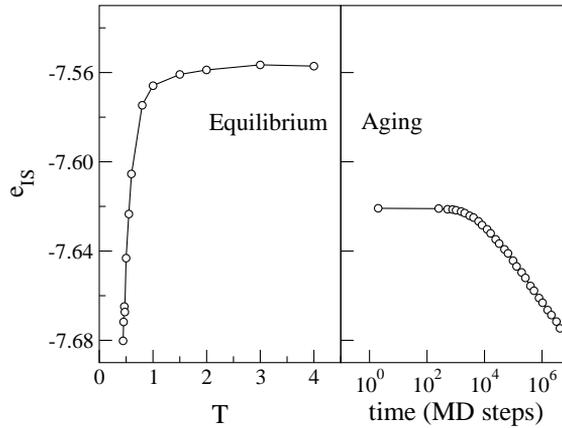


Fig. 1. The IS energy in an equilibrium situation (left) as a function of temperature, and in an aging computation (right) as a function of time, following a  $T$  jump from  $T = 0.8$ – $0.25$ .

absolute ordered minimum corresponding to the crystalline state, and the lower disordered state to the corresponding ideal glass state. The PES is obviously independent of temperature, but the way the energy landscape is sampled by the system depends on the value of  $T$ . In particular at high temperatures the system essentially samples the numerous shallow local minima, and when  $T$  is decreased deeper and deeper minima are reached, up to the point where the system remains trapped in one of them. At this point one can distinguish in the dynamics an intra- and an inter-basin motion, according to the possibility for the representative point to leave the IS or not, respectively. As the temperature is lowered the time scales associated with the two motions become well separated, and this trend continues for values of  $T$  in the vicinity of  $T_{MCT}$ . Another indication of the dynamical scale separation comes from the typical behavior of the density time correlation function in the MCT region, where the temporal regimes (called  $\alpha$  and  $\beta$  relaxation) are usually clearly distinct. Therefore we expect that the dynamics of a supercooled liquid can be considered as the combination of a fast intra-basin stage at short times, corresponding to vibrations in a potential well, and a slow inter-basin stage for longer times, when the system is attempting a change of configuration passing from an IS to another.

We have studied a model system which allows a careful dynamical analysis. The model is a binary mixture of Lennard Jones particles (BMLJ), which has been extensively studied in the past [15]. The model has been optimized to prevent crystallization. The BMLJ is a (80:20) binary mixture of particles of types A and B. Details of the interaction potential can be found in Ref. [15]. We have studied the isochore with number density  $n = 1.2$  and simulation times up to  $6 \times 10^7$  integration time steps. A sample of equilibrium configurations were used in order to obtain the local energy minima via a quenching procedure. The critical temperature of MCT for this system is 0.435 [15].

The results of the equilibrium numerical computation are reported in Fig. 1 (left panel), where the average IS energy  $e_{IS}$  is reported for various  $T$  values. As

expected, the energy remains roughly constant at high  $T$ , then rapidly decreases on lowering  $T$  [16].

#### 4. Thermodynamic description of the inherent structures

The decomposition of the system partition function  $Z_N(T)$  into a sum of contribution from the IS with energy  $e_{IS}$  is given by [13]

$$Z_N(T) = \sum_{e_{IS}} \Omega(e_{IS}) \exp[-\beta\{e_{IS} + f_v(e_{IS}, T)\}], \quad (3)$$

where  $\Omega(e_{IS})$  is the density of basin of depth  $e_{IS}$  and the vibrational free energy  $f_v$  is the vibrational free energy, within a basin, averaged over all basins of depth  $e_{IS}$ .

The configurational  $S_c$  entropy is related to  $\Omega(e_{IS})$ , the number of states with energy  $e_{IS}$ , by the relation

$$S_c = k_B \ln \Omega(e_{IS}). \quad (4)$$

If we introduce the basin free energy  $f_b(e_{IS}, T) = e_{IS}(T) + f_v(e_{IS}, T)$  and perform a minimization in  $e_{IS}$  of

$$F(T) = f_b(e_{IS}, T) - TS_c(e_{IS}), \quad (5)$$

we get in the thermodynamic limit the free energy  $F$ . The first term takes into account the basin depth and shape, the second one the number of basins with energy  $e_{IS}$ .

Separating  $f_b(e_{IS}, T)$  in its energetic and entropic contribution, the configurational entropy can be calculated as the difference between the liquid entropy and the entropy of the system constrained in an IS [17–19]. In the experimental procedure commonly adopted to evaluate  $S_c$ , the vibrational entropy is identified with the entropy of the stable crystal since the vibrational properties of a system constrained in a deep basin are often similar to the properties of the close crystalline structure.

Once the  $T$  dependence of the IS is known, the entropy of the liquid can be calculated via thermodynamic integration starting from the ideal gas binary mixture reference point, along an isotherm, up to the studied density. To estimate the basin entropy, we assume that at the lowest studied  $T$ , the unknown  $f_b(e_{IS}, T)$  can be approximated by the harmonic free energy of a disordered system characterized by the eigenfrequencies spectrum calculated from the IS at the corresponding  $T$ . The results are reported in Fig. 2 both as a function of the IS energy and temperature. The extrapolations, obtained using the known power-law behavior derived from density functional theory [20], are also shown. Note that, *if the extrapolations are reliable*, the configurational entropy vanishes at  $T=0.297\pm 0.01$ , which defines the Kauzmann temperature  $T_K$  for the BLJM.

#### 5. Aging

The separation of fast and slow time scales in the dynamics of supercooled liquids not only influences their equilibrium properties, but has also important consequences on

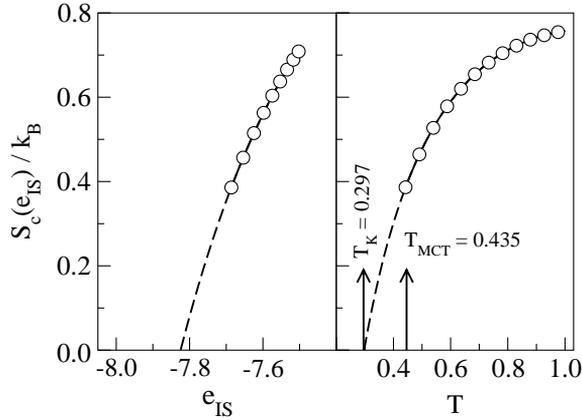


Fig. 2. The configuration entropy as a function of the IS energy (left) and temperature (right).

their out-of-equilibrium behavior. In particular, the slow and fast degrees of freedom tend to reach an equilibrium situation on their respective time scales, to which different temperatures correspond. On the same BLJM we perform an instantaneous temperature quench from  $T_i$  to  $T_f$ , then measure, in the same way as in equilibrium, the behavior of the IS energy. The result is reported in Fig. 1 (right). We have made the hypothesis that the free energy expression we used in equilibrium can be extended to aging situations [21].  $F(T)$  has a vibrational part unambiguously given by  $f_b(e_{IS}(t_w), T_{bath})$ , since the intrabasin degrees of freedom quickly equilibrate with the thermostat at  $T_{bath}$ . Here  $t_w$  is the time since the quench. The entropic contribution to the free energy requires the definition of a temperature, which we call internal  $T_{int}$ , higher than the thermostat temperature [22,23], to reflect the out-of-equilibrium condition and the slow flow of heat from the system to the thermostat. Contrary to the equilibrium case, the system selects the internal temperature but it is constrained to basins of depth  $e_{IS}(t_w)$ . Hence, the internal temperature  $T_{int}(e_{IS}, T_{bath})$  selected by the system when it is populating basins of depth  $e_{IS}$  is a solution of the minimization equation for the free energy, but with the value  $e_{IS}$  fixed, i.e.,

$$T_{int}(e_{IS}, T_{bath}) = \frac{(\partial/\partial e_{IS})f_b(T_{bath}, e_{IS})}{(\partial/\partial e_{IS})S_c(e_{IS})}. \quad (6)$$

Note that  $f_b$  is now evaluated at the thermostat temperature  $T_{bath}$ . This expression for  $T_{int}$  coincides with the expression proposed by Franz and Virasoro [24] in the context of p-spin systems.

The  $T_{int}$  calculated theoretically according to Eq. (6) has been compared with a numerical experiment designed to independently calculate the temperature of the configurational subsystem, i.e., by calculating the ratio between decay of correlation in thermal equilibrium and response to an external perturbation. Linear response theory predicts that, in equilibrium, under suitable choice of the perturbation, this ratio is the temperature. We chose as perturbation  $(\rho_{\mathbf{k}}^\alpha + \rho_{-\mathbf{k}}^\alpha)$ , where  $\rho_{\mathbf{k}}^\alpha \equiv \sum_i^{N_x} e^{i\mathbf{k}\cdot\mathbf{r}_i^\alpha}/\sqrt{N}$  is the

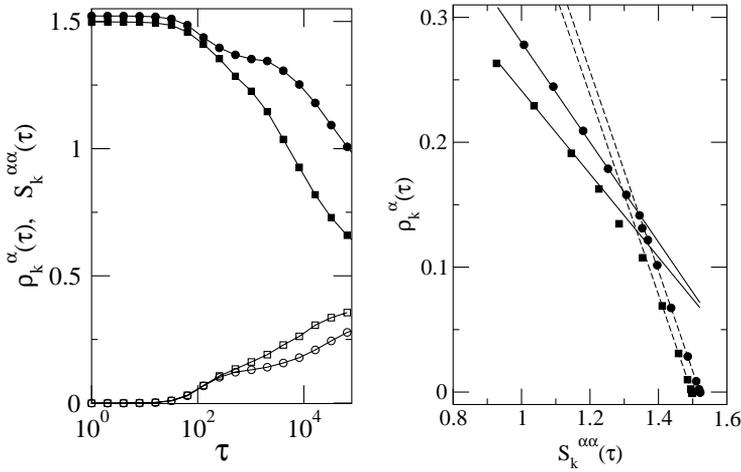


Fig. 3. Left: time dependence of the response ( $\rho_k^\alpha$ , open symbols) and correlation function ( $S_k^{\alpha\alpha}$ , filled symbols) for waiting time  $t_w = 1024$  (circles) and  $t_w = 16384$  (squares). Right: Corresponding parametric plot of  $\rho_k^\alpha$  vs.  $S_k^{\alpha\alpha}$  for the two studied  $t_w$ . Dashed lines have slope  $V_0/k_B T_{bath}$  (with  $T_{bath} = 0.25$ ), solid lines have slope  $V_0/k_B T_{int}(e_{IS}(t_w = 1024) = -7.576, T_{bath} = 0.25)$  and  $V_0/k_B T_{int}(e_{IS}(t_w = 16384) = -7.602, T_{bath} = 0.25)$ .  $k$  is 6.7.

Fourier transform of the density of  $\alpha$  particles at wavevector  $\mathbf{k}$ , and study the response of  $\rho_{\mathbf{k}}^\alpha$ , related to the dynamical structure factor  $S_{\mathbf{k}}^{\alpha\alpha}(t) \equiv \langle \rho_{\mathbf{k}}^\alpha(t) \rho_{-\mathbf{k}}^\alpha(0) \rangle_0$  by

$$\langle \rho_{\mathbf{k}}^\alpha(\tau) \rangle = -\frac{V_0}{k_B T} [S_{\mathbf{k}}^{\alpha\alpha}(\tau) - S_{\mathbf{k}}^{\alpha\alpha}(0)]. \tag{7}$$

This calculation, reported in Ref. [21] has confirmed that in the time window where the decay of correlation is controlled by intrabasin dynamics the calculated temperature is equal to the bath temperature. In the region where the decay of correlation is controlled by the inter-basin motion, the calculated temperature agrees very well with the theoretical prediction for  $T_{int}$ , as shown in Fig. 3. At short time (intra-basin motion)  $\langle \rho_{\mathbf{k}}^\alpha(t) \rangle$  vs.  $S_{\mathbf{k}}^\alpha(t)$  is linear with the expected  $T_{bath}^{-1}$  slope, properly describing the equilibrium condition of the vibrational dynamics with the external reservoir. At larger times, the inter-basin motion sets in and the slopes of  $\langle \rho_{\mathbf{k}}^\alpha(\tau) \rangle$  vs.  $S_{\mathbf{k}}^{\alpha\alpha}(\tau)$  are extremely well predicted by the values of  $T_{int}$  calculated according Eq. (6). In conclusion, the extension of the thermodynamics formalism to the case of an out-of-equilibrium supercooled liquid allows to predict the response of the aging system to an external perturbation and the way this response depends on the time spent in the low-temperature glassy state.

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