INTRODUCTION

The concept of fragility provides a possibility to rank different supercooled liquids on the basis of the temperature dependence of dynamic and/or thermodynamic quantities. We recall here the definitions of kinetic and thermodynamic fragility proposed in the last years and discuss their interrelations. At the same time we analyze some recently introduced models for the statistical properties of the potential energy landscape. Building on the Adam-Gibbs relation, which connects structural relaxation times to configurational entropy, we analyze the relation between statistical properties of the landscape and fragility. We call attention to the fact that the knowledge of number, energy depth and shape of the basins of the potential energy landscape may not be sufficient for predicting fragility. Finally, we discuss two different possibilities for generating strong behavior.

Soon after the introduction of the concept of "topographic view of the Potential Energy Landscape (PEL)" [1,2], it became immediately clear that a key role in controlling the kinetic arrest characterizing the glass transition was played by the number of distinct PEL local minima (inherent structures), \( \Omega_N \), and by their energy distribution, \( \Omega_N(E) \). Indeed, it was suggested that the qualitatively different behavior of different supercooled liquids could be traced back to the difference in the \( \Omega_N \) function, or, more specifically to the steepness of the \( N \) dependence of this quantity. From general arguments, in a mono-component collection of a large number, \( N \), of units (atoms, molecules, ...), it can be shown that \( \Omega_N \sim \exp(\alpha N) \). Similarly, it holds \( \Omega_N(E) \sim \exp(\Sigma(e)/kB) \). Here \( \Sigma(e) \) assumes the meaning of "configurational entropy" and it is an extensive function of the energy per particle \( e = E/N \). The quantity \( \alpha = \max_{\Sigma(e)}(\Sigma(e))/Nk_B \) is a measure of the total number of "inherent structure" (individual minima of the potential energy hyper-surface). In comparing the behavior of different glass forming systems, particular emphasis is placed in the relation existing between \( \alpha \) and the "fragility" of the system under investigation.

The "fragility" concept, in its modern form, has been introduced, developed and widespread by Angell [4]. It describes, in its kinetic version, how fast the structural relaxation time \( \tau_\alpha \) increases with decreasing temperature on approaching the glass transition temperature, \( T_g \), defined as the temperature where \( \tau_\alpha \) becomes equal to 100 s. "Strong" systems (low values of fragility) show a "weak" \( T \)-dependence of \( \tau_\alpha(T) \), which can be described by an Arrhenius law \( (\tau_\alpha(T) = \tau_\infty \exp(\Delta/k_BT)) \) while "Fragile" systems show -close to \( T_g \)- a much faster \( T \)-dependence of the relaxation time, which is also markedly non-Arrhenius (this dependence could be, for example, described by a \( T \)-dependence of the activation energy \( \Delta \)). The relaxation time is a quantity which is rather difficult to access, in particular when the value of \( \tau_\alpha \) is large, and, moreover, it seems also to be technique-dependent.

For these reasons, in non-polymeric liquids, the fragility is usually defined through the \( T \) dependence of the shear viscosity, \( \eta \). This choice leads to a first ambiguity, especially in comparing different systems, as the fragility defined through \( \tau_\alpha(T) \) and that defined through \( \eta(T) \) are not coincident. This can be rationalized by recalling the Maxwell relation, \( \eta=G_\infty \tau_\alpha \) (here \( G_\infty \) is the infinite frequency shear modulus of the liquid), and recalling that \( G_\infty \) at \( T_g \) spans over about two decades among different systems. Another possible definition of fragility comes from the temperature dependence of the mass diffusion coefficient. In this case, according to the Stokes-Einstein relation \( (D = k_B T/(6\pi \eta r)) \), being \( r \) the effective hydrodynamic radius, it is the mobility \( \mu = (D/T) \) that is (inversely) proportional to the viscosity and, therefore, must be analyzed. Once more, it should be expected that the fragility defined via mobility and that defined via viscosity are not coincident. Indeed, i) the effective hydrodynamic radius may have a temperature dependence and ii) it is well known that in supercooled liquid at low temperature the "decoupling" phenomenon (the failure of the Stokes Einstein relation) occurs. In the recent years, the fragility has been quantified according to the \( T \) behavior of \( \eta \), but this has been done following different prescription (vide infra).

Despite minor ambiguities introduced by its different definitions, the concept of fragility has a deep influence on the study of relaxation processes in supercooled liquids. Many studies have evidenced the existence of correlations between the values of the fragility and other properties of the supercooled liquids, such as: i) the "visibility" of the Boson Peak [8]; ii) the \( T \)-dependence of the shear elastic modulus in liquids (shoving model) [8-11]; iii) the stretching of the decay of the correlation functions at the glass transition temperature [12-13]; iv) the nonlinearity of the relaxation functions [14] and, very recently, v) the vibrational properties of the glass at \( T \to 0 \) [15]. Other works have tried to extract physical information on the nature of the glass transition from the
existence of these correlations \cite{16,17}. Finally, we recall a recent attempt to extend the dimensionality of the space spanned by the fragility index. Instead of using a single value to classify the $T$-dependence of the viscosity, Ferrer et al. \cite{18} proposed to associate two indexes to every glassformer. The first index (fragile/non-fragile) measures how much the viscosity is Arrhenius-like at low temperature while the second one (strong/weak) does the same around the melting point. A deeper discussion on the correlation between fragility and other supercooled liquid properties can be found in Ref. \cite{19}.

The relation between the statistical properties of the landscape and the fragility is thought to be a central issue in the comprehension of the physics behind the glass transition. Debenedetti and Stillinger \cite{20} state in a very recent review: "Equally important is the translation of qualitative pictures ... into precise measures of strength and fragility based on the basin enumeration function". A first connection between the fragility and the topographic differences in the energy landscape is found in Ref. \cite{21}. There the landscapes of strong liquids were supposed to have a "uniform" roughness, while a twolengthscale arrangement of the minima -with the introduction of the meta-basins, a concept that has been recently revitalized by Doliwa and Heuer \cite{22} - was expected to characterize the PEL of fragile liquids. In 1995, Angell \cite{23}, rationalizing the much larger specific heat jump at the glass transition shown by the fragile liquids with respect to the strong ones, concluded that "Fragile liquids would have high density of minima per unit energy..." and "Surfaces with few minima ... generate strong liquids...". Similar conclusions are reported in Ref. \cite{24} and by Debenedetti and Stillinger \cite{20}, who, more recently, wrote that "... strong landscape may consist of a single metabasin whereas fragile ones display a proliferation of well-separated metabasin".

Summing up, there seems to be consensus on the statements

$$\text{strong systems} \iff \text{small } \alpha$$

$$\text{fragile system} \iff \text{large } \alpha$$

An attempt to determine a quantitative relation between fragility and number of states on a theoretical basis, within the framework of the "gaussian landscape model" (see below), is due to Speedy \cite{25}, who derived a direct proportionality between kinetic fragility and $\alpha$. This relation has been then criticized by Sastry \cite{26}, who -again using the gaussian model to fit his molecular dynamics simulation of the Kob-Anderson Lennard Jones Binary Mixture (BMLJ) at different densities- reached the conclusion of a proportionality between fragility and the square root of $\alpha$.

In this paper we first present a summary of the different definitions of "fragility" that are commonly used in the current literature, and then recall several models of configurational entropy (several "landscapes") proposed in the past that -with the help of the Adam-Gibbs equation, or of the Vogel-Tamman-Fulcher relation, or both- lead to different expression for the fragility in terms of the parameters characterizing the "landscapes". In the subsequent sections, we review the Speedy and the Sastry propositions on the $\alpha$- dependence of the fragility for the examined landscapes. Finally we emphasize that landscapes with the same statistical properties (i.e. same total number of basins, same energy distribution of the basins depth) may be characterized by different fragilities, calling attention on the role of the different parameters entering in the Adam- Gibbs expression. We conclude discussing the obtained results in the context of the strong-to-fragile transition observed in some strong glass forming liquids.

\section*{FRAGILITIES}

As discussed in the introduction, and following Angell \cite{4}, we will define the kinetic fragility in terms of the temperature behavior of the viscosity and not of the structural relaxation time. Having clarified this point, however, we have to face -for the present purpose- different definitions of the "index of (kinetic) fragility". The robustness of a concept like the fragility lies in the observation that -when plotting $\log(\eta(T))$ vs. $T/T_g$- the curves for different liquids (beside very few exceptions) do not intersect each other, and converge to a common point at $T = T_g$ (by definition) and at $T \to \infty$. Given this situation, it is possible to sort the systems, i.e. to unambiguously asses whether or not a system is more fragile than another. It is, therefore, natural to assign a numerical value to this concept: the index of fragility.

\subsection*{Kinetic fragility: local definitions}

The first definition, let’s call it "Angell’s kinetic fragility", $m_A$, is

$$m_A = \frac{d \log(\eta(T)/\eta_\infty)}{d(T_g/T)} \bigg|_{T=T_g}$$

Here $\eta_\infty$ is the limiting high temperature viscosity and $T_g$ is defined from the condition $\eta(T_g) = 10^{13}$ poise. As it is experimentally observed that all the liquids share a very similar value of $\eta_\infty \approx 10^{-4}$ poise, this quantity is conventionally fixed to this value. Accordingly, an ideal strong glass (strictly Arrhenius behavior) would have $m_A \approx 17$, whereas higher values are indication of higher fragility.

While in principle there is no upper limit for $m_A$, on a practical ground the most fragile systems seems to be tri-phenyl-phosphate, with $m_A \approx 160$. 
A very similar definition has been proposed by Speedy

\[ m_s = \frac{d \left[ \frac{\log(\eta(T)/\eta_\infty)}{\log(\eta(T)/\eta_\infty)} \right]}{d(T_g/T)} \bigg|_{T=T_g} \]  

(2)

At a first sight, it seems that a trivial normalization factor would bring from \( m_s \) to \( m_A \). However, this expression become more useful than Eq. 1 if we want to relax the assumption \( \eta_\infty = 10^{-4} \) poise. In conjunction with Eq. 2 it is also useful to define the glass transition temperature \( T_g \) as the temperature where \( \eta(T_g)/\eta_\infty = 10^{17} \); we will use this definition hereafter. As we will see below, if we aim to study, for example, the density dependence of the fragility of a given system, it will be easier to use Eq. 2 where the density dependence of \( \eta_\infty \), although small, has been washed out. It is worth to point out, however, that for all the practical purposes, when dealing with the experimental data the difference in using Eq. 1 or Eq. 2 is by all means irrelevant (apart from a trivial factor very close to 17). The fragility index \( m_r \) ranges from one for strong glasses to \( \approx 10 \) for the more fragile systems.

The previous two definitions focus on the behavior of \( \eta(T) \) at the glass transition temperature. More recently, another index of fragility—often referred to as \( F_{1/2} \)—has been introduced by Richert and Angell [27] to “measure” the fragility at intermediate temperature (see also the discussion in Ref. [28]). Naming \( T^* \) the temperature that satisfies \( \log(\eta(T^*)) = \log(\eta(T_g)) + \log(\eta(T_\infty))/2 \) (i.e. the temperature where the viscosity is halfway -in logarithmic scale- between \( \eta_\infty \) and \( 10^{13} \) poise), \( F_{1/2} \) is defined as \( F_{1/2} = 2(T_g/T^*) - 1 \). It is worth to mention that \( F_{1/2} \) and \( m_A \) (or \( m_s \)) do not provide “exactly” the same information: a plot of one quantity against the other does not indicate a perfect correlation, rather it shows a scatter of the points around an average trend [29]. The existence of such a scattering has been recently rationalized by Chandler and Garrahan within the framework of a coarse-grained model of glass formers [30].

Finally, a generalized, temperature dependent fragility (either \( m_A \) or \( m_s \)) is sometime introduced, using equations similar to Eqs. 1 or 2 where \( T_g \) is substituted by a generic reference temperature \( T \). We will call these quantities \( m_A(T) \) and \( m_s(T) \), with the implicit definition that when the argument is missing, the quantities are calculated at \( T = T_g \).

**Kinetic fragility: global definitions**

The previous indexes of fragility were associated to the behavior of \( \eta(T) \) at a given temperature. Other definitions are based on the global behavior of the viscosity, and necessarily rely on the existence of a functional expression for \( \eta(T) \).

A global definition of kinetic fragility arises from the experimental observation that the temperature dependence of the viscosity follows rather closely a Vogel-Tamman-Fulcher (VTF) law [31]:

\[ \eta(T) = \eta_\infty \exp\left( \frac{DT_g}{T-T_o} \right). \]

(3)

where \( \eta_\infty \), \( D \) and \( T_o \) are system dependent parameters. As long as the VTF description of \( \eta(T) \) is correct, one of the two parameters in the argument of the exponential can be eliminated in favor of \( T_g \) as -from the definition of glass transition temperature- the following relation holds [3]:

\[ T_g = T_o(1 + \frac{D}{17 \ln(10)}) \]

(4)

Plugging Eq. 3 in Eq. 2 and using Eq. 4 one gets that the parameter \( D \) is related to the previously defined fragilities:

\[ D = \frac{17 \ln(10)}{m_s - 1} \]

(5)

and, therefore, can be assumed to be a further fragility index. This index, which ranges from \( \infty \) for strong liquids (actually \( D \approx 100 \) for vitreous silica) to \( \approx 5 \) for the fragile ones, is in same sense "weaker" than the other three previously introduced, as its validity is based on the assumed \( T \)-dependence of the viscosity (Eq. 3).

The assumption of the validity of the VTF law for the viscosity also leads to a relation between the local fragility defined at different temperatures. Indeed, recalling the definition of \( F_{1/2} \) and Eq. 2 one gets [27]

\[ F_{1/2} = \frac{m_s - 1}{m_s + 1} \]

(6)

**Thermodynamic fragility**

An important step forward in relating the fragility with the PEL properties has been certainly achieved with the introduction of the "thermodynamic fragility" [32]. Similarly to the kinetic fragility which naturally emerges from the Angell plot (\( \log(\eta) \) vs. \( T_g/T \) for different systems), the vigor of the concept of thermodynamic fragility arises from the temperature dependence of the excess entropy \( S_{ex} \), defined as the difference between the entropy of the liquid and the entropy of the stable crystal. On plotting \( S_{ex}(T_g)/S_{ex}(T) \) vs. \( T_g/T \), one obtains a plot very similar to the Angell plot, where the different systems stand in the same order [33].

In similar fashion to the kinetic fragility \( F_{1/2} \), it has been defined a "thermodynamic" fragility \( F_{3/4} \): naming \( T^* \) the temperature where \( S_{ex}(T_g)/S_{ex}(T) = 3/4 \), i.e. the temperature where the inverse excess entropy equals...
3/4 of its \( T_g \) value, \( F_{3/4} \) is defined as \( F_{3/4} = 2(T_g/T^*) - 1 \). In this case, the value 3/4, and not 1/2, has been chosen because of the difficulties associated to determine the excess entropy at high \( T/T_g \) in strong liquids. In a recent paper Martinez and Angell \[32\] have shown that it exists a remarkable correlation between \( F_{1/2} \) and \( F_{3/4} \); with few exceptions it turns out that \( F_{1/2} \approx F_{3/4} \) within 10%. This observation rationalizes the well known fact that the amplitude of the specific heat jump at \( T_g \) is linked to the fragility, but also points out that is not the specific heat jump alone, but rather this jump divided by the excess entropy at \( T_g \), that is actually related to \( m_s \).

In analogy with \( m_s \) (or with \( m_\alpha \)) it would be natural to define a further index of the thermodynamic fragility as the derivative at \( T_g \) of the inverse reduced excess entropy with respect to the inverse reduced temperature. To our knowledge, this index has not been yet introduced, but -as we will see below- this quantity naturally appears when the Adam-Gibbs relation is used to work out a link between kinetic and thermodynamic fragility. It is useful, therefore, to introduce this thermodynamic fragility (\( m_T \)) index as:

\[
m_T \equiv \frac{d(S_{ex}(T_g)/S_{ex}(T))}{d(T/T_g)} \bigg|_{T=T_g} = T_g \frac{S_{ex}'(T_g)}{S_{ex}(T_g)},
\]

being \( S_{ex}'(T) \) the temperature derivative of \( S_{ex}(T) \).

**Relation between kinetic and thermodynamic fragility**

The Adam-Gibbs equation \[34\] establishes a relation between the structural relaxation time and the configurational entropy \( \Sigma(T) \):

\[
\tau(T) = \tau_\infty \exp \left( \frac{\mathcal{E}}{T \Sigma(T)} \right)
\]

or, relying on the Maxwell relation, between the viscosity and the configurational entropy:

\[
\eta(T) = \eta_\infty \exp \left( \frac{\mathcal{E}}{T \Sigma(T)} \right)
\]

where \( \tau_\infty \) (\( \eta_\infty \)) is the usual infinite temperature limit for the relaxation time (viscosity) and \( \mathcal{E} \) a system dependent parameter with the physical dimension of an energy that is somehow related to the energy barrier for activated processes. This equation is the key relation that allows us to create a link between kinetic and thermodynamic fragility and, ultimately, via the configurational entropy a link between kinetic fragility and the statistical properties of the PEL. Let us first observe that, as the energy barrier is expected to have a weak and smooth temperature behavior and not to diverge at any temperature, according to Eq. \[9\] the viscosity diverges at the temperature (Kauzmann temperature \( T_K \)) where the configurational entropy vanishes. If both the Adam-Gibbs (Eq. \[9\]) and Vogel-Tamman-Fulcher relations (Eq. \[8\]) are valid, then necessarily \( T_o \) and \( T_K \) are equal one to each other. This equality has been recently disputed \[37\]. We do not further discuss this problem, with the aim to study the mathematical consequences of the different landscape models introduced in the literature, we will assume (when necessary) that \( \mathcal{E} \) is a slowly varying smooth function of \( T \) (thus, that \( T_o = T_K \)). It must also be noted that the thermodynamic fragility is defined through the experimentally accessible *excess* entropy, while the Adam-Gibbs relation calls into play the *configurational* entropy. In the following we will not make difference between the two entropies, relying upon the observation that configurational and excess entropy seems to be actually proportional to each other \[34\], even if other studies indicate the failure of such a proportionality \[37\]. Assuming that the Adam-Gibbs relation correctly describes the \( T \) dependence of \( \eta \) in a supercooled liquids, by plugging Eq. \[9\] into the definition of \( m_s \), Eq. \[2\] we get:

\[
m_s = 1 + T_g \frac{\Sigma'(T_g)}{\Sigma(T_g)},
\]

and, recalling Eq. \[7\] we have the desired relation between kinetic and thermodynamic fragility:

\[
m_s = 1 + m_T.
\]

Equation \[10\] also constitutes the basis to obtain a link between the kinetic fragility \( m_s \) and the number of states \( \alpha \). Indeed, recalling the relation \( \alpha = \max_e \{ \Sigma(e(T)) \} / N k_B \), if we know -or have a model for- the configurational entropy of a given system, we could determine \( \alpha \) and \( m_s \), and thus try to relate one to the other.

**MODELS OF LANDSCAPE**

In this section we will briefly recall the main models that have been introduced in the recent literature to represent the configurational entropy of supercooled liquid systems. In the first three subsections we elucidate models of configurational entropy and derive the relations between the different quantities of interest (\( T \) and \( e \) dependence of \( \Sigma \), fragility, etc.) with the specific hypothesis that the vibrational entropy associated to a specific minimum of the PEL is independent from its energy elevation. In the following subsection, we relax this hypothesis, assuming a linear dependence of the vibrational free energy from \( e \), and showing how the equations relating the relevant physical quantities to the configurational entropy parameters are modified.
Gaussian model

The gaussian model is at the basis of the interpretation of the configurational entropy in simulated supercooled liquids. After the first studies \cite{38, 39, 40}, the gaussian model has been chosen to describe quantitatively the energy dependence of $\Sigma(e)$ in different systems \cite{25, 26, 41, 42, 43}. According to this model, an explicit functional form ( gaussian) for $\Omega_N(E)$ - the energy distribution of the minima of the PEL - is assumed,

$$\Omega_N(E) = \exp(\alpha N) \exp\left[\frac{(E - E_o)^2}{\epsilon^2}\right], \quad (12)$$

From this equation, the configurational entropy of the gaussian model becomes ($e = E/N$):

$$\Sigma(e) = k_B N \left[ \alpha - \frac{(e - e_o)^2}{\epsilon^2} \right] \quad (13)$$

being $\bar{\epsilon} = \epsilon/\sqrt{N}$. In this expressions $\alpha$ counts the total number of states (it is the maximum of $\Sigma(e)/N$ in $k_B$ units), $e_o$ is an irrelevant parameter (it fixes the zero of the energy scale) and $\bar{\epsilon}$ is the width of the distribution. In order to express the configurational entropy as a function of the temperature, we must first determine the energy of the minima of the PEL populated at a given temperature. Using \cite{14, 15}

$$\frac{1}{T} = \frac{d\Sigma(e)/N}{de} \quad (14)$$

we get

$$e(T) = e_o - \frac{\epsilon^2}{2k_B T} \quad (15)$$

and, finally, inserting Eq. (14) into Eq. (13) we have the explicit expression of the configurational entropy as a function of the temperature:

$$\Sigma(T) = k_B N \left[ \alpha - \frac{\epsilon^2}{(2k_B T)^2} \right] \quad (16)$$

From Eq. (16) the Kauzmann energy $e_K$, i.e. the energy where $\Sigma(e) = 0$, is promptly derived:

$$e_K = e_o - \bar{\epsilon}\sqrt{\alpha} \quad (17)$$

and, plugging the Kauzmann energy (Eq. (17)) in Eq. (14) we find the Kauzmann temperature:

$$k_BT_K = \frac{\bar{\epsilon}}{2\sqrt{\alpha}} \quad (18)$$

It is useful to eliminate $\bar{\epsilon}$ from the expression of the configurational entropy (in its explicit $T$-dependent expression) in favor of $T_k$, using Eq. (18) so to obtain:

$$\Sigma(T) = k_B N \alpha \left[ 1 - \frac{T_k^2}{T^2} \right] \quad (19)$$

Once we have a model for the configurational entropy, we can - applying Eq. (19) - find an expression for the fragility in terms of the parameters of the model itself. As parameters, we have the freedom to choose among ($\alpha$, $\bar{\epsilon}$, $T_K$, $e_K$). One compact possibility, which has the advantage to explicitly depend only on $T_K$, is:

$$m_s = \frac{T_g^2 + T^2}{T_g^2 - T^2} \quad (20)$$

In this expression, $T_g$ appears explicitly and cannot be eliminated because in the gaussian model (a pure thermodynamic model) the dynamics is not defined and therefore $T_g$ must be regarded as a parameter external to the theory. Other possible selection of parameters, and thus other expressions for the fragility, are of course possible. Eq. (20) (as well as similar expressions for other landscape models, see below) makes clear the well know fact that the fragility is somehow related to the "distance" between $T_g$ and $T_K$: the higher is the ratio $T_g/T_K$ the strongest is the liquid.

As finally remark, we observe how - having imposed the validity of both the Adam-Gibbs relation and the gaussian model for the configurational entropy - the temperature dependence of the viscosity turns out to be controlled by the law:

$$\eta(T) = \eta_\infty \exp\left(\frac{DT_K}{T - T_K} \frac{T}{T + T_K}\right), \quad (21)$$

with $D = E/(\alpha N k_B T_K)$, which is different by a VTF relation. In other words, the VTF law, the Adam-Gibbs relation and the gaussian model cannot be simultaneously invoked (especially when the shape of the PEL basins is independent on the depth). Equation (21) can be regarded as a VTF law with a temperature dependent coefficient $D'(T) = DT/(T + T_k)$. In the high $T$ limit ($T >> T_k$), $D' \rightarrow D$ while in the low $T$ regime ($T$ approaching $T_k$) $D' \rightarrow D/2$.

Hyperbolic model

For thirty years it has been realized \cite{46} that the temperature dependence of the (constant volume) excess specific heat can be described by a hyperbolic law ($C \approx const + const'/T$), and this law is commonly used to represent the experimental data \cite{25}. The "landscape model" that gives rise to such a temperature dependence for the excess specific heat is the so called hyperbolic model, recently introduced and discussed in detail by Debenedetti, Stillinger and Lewis \cite{17}. In Ref. \cite{17}, the model is derived from the assumption of a hyperbolic temperature dependence of the "configurational" heat capacity, and (assuming the validity of the Adam-Gibbs relation), it implies as a mathematical consequence the validity of the VTF relation. For simplicity, here we prefer
to start assuming the mathematical validity of both the Adam-Gibbs and the VTF, the hyperbolic temperature dependence of the excess specific heat results as consequence. Obviously, as discussed in [13], the two routes are equivalent. It is worth to point out that the "gaussian landscape" is named after the $e$-dependence of the number of states, while the "hyperbolic landscape" is named after the $T$ behaviour of the specific heat [27], a rather different quantity. It is our aim to write down the main expressions for this model using the same notation of the previous section, and to extract the equations for the fragilities. By comparing Eq. [23] and [24] it turns out an explicit temperature dependence for $\Sigma(T)$:

$$\Sigma(T) = \frac{\mathcal{E}}{DT_K} \left[ 1 - \frac{T_K}{T} \right]$$  \hspace{1cm} (22)

It is implicit in this expression the coincidence of $T_o$ and $T_K$. This equation can be cast in form very similar to Eq. [18] by defining the quantities $\alpha$ and $\bar{\epsilon}$:

$$\alpha \equiv \frac{\mathcal{E}}{DNk_BT_K},$$  \hspace{1cm} (23)

$$\bar{\epsilon} \equiv \frac{2\mathcal{E}}{DN} = 2k_BT_K\alpha,$$  \hspace{1cm} (24)

As we will see soon, $\alpha$ and $\bar{\epsilon}$ play here the same role as they have in the gaussian model, therefore the first equation is a link between the "number of states" and the constants entering in the AG ($\mathcal{E}$) and VTF ($D$ and $T_K$) relations. The second equation can be compared to Eq. [18] where $\sqrt{\alpha}$ appears instead of $\alpha$. Rewriting Eq. [22] with the elimination of $\mathcal{E}$ and $D$ in favor of $\alpha$ and $\bar{\epsilon}$, we have:

$$\Sigma(T) = k_BN \left[ \alpha - \frac{\bar{\epsilon}}{2k_BT} \right],$$  \hspace{1cm} (25)

an expression that can be directly compared with Eq. [18] or, expressing the pre-factor in Eq. [22] in terms of $\alpha$ via Eq. [23]

$$\Sigma(T) = k_BN\alpha \left[ 1 - \frac{T_K}{T} \right],$$  \hspace{1cm} (26)

that can be compared with Eq. [19]

At variance with the gaussian model, where we started with a model for $\Sigma(e)$ and derived $\Sigma(T)$, we now have a model for $\Sigma(T)$. To obtain an expression for $\Sigma(e)$ we first derive the temperature dependence of the energy of the minima visited by Eq. [14]

$$e(T) = e_R + \int_{T_R}^{T} T \frac{d\Sigma}{dT} dT$$  \hspace{1cm} (27)

$$= e_R + \alpha k_BT_K \ln \left( \frac{T}{T_R} \right)$$

where $e_R$ and $T_R$ are integration constants whose values, as we will see, are not relevant for the interesting physical quantities. Inverting Eq. [27] and plugging the resulting $T(e)$ into Eq. [26] we get:

$$\Sigma(e) = Nk_B\alpha \left[ 1 - \frac{T_K}{T_R} \exp \left( - \frac{2(e - e_R)}{\bar{\epsilon}} \right) \right]$$  \hspace{1cm} (28)

Obviously, we can eliminate $T_R$ from this equation, by properly redefining $e_R$. A useful possibility is to choose $T_R = T_K$, then, from Eq. [27], $e_R = e_K$ and:

$$\Sigma(e) = Nk_B\alpha \left[ 1 - \exp \left( - \frac{2(e - e_K)}{\bar{\epsilon}} \right) \right].$$  \hspace{1cm} (29)

At variance with the configurational entropy of the gaussian model, the present $\Sigma(e)$ does not show any maxima, rather it increase continuously, asymptotically approaching the value $Nk_B\alpha$.

From Eq. [26] using Eq. [10] we can easily determine the fragility of this model:

$$m_s = \frac{T_g}{T_g - T_K}.$$  \hspace{1cm} (30)

It is worth to point out that this expression is the expansion of the fragility of the gaussian model to first order in $T_g - T_K$.

**Logarithmic (or binomial) model**

The previous two models for the configurational entropy share the property that $d\Sigma/de$ is non diverging at $e = e_K$, so the Kauzmann temperature exists and it is non-vanishing. In order to introduce a more flexible model, embedding the possibility of having a vanishing Kauzmann temperature, Debnedetti, Stillinger and Shell [14] recently proposed a modification of the gaussian model, that, with a slight change in notation with respect to the original definition, reads:

$$\Sigma(e) = Nk_B\alpha \left\{ (1 - \gamma) \left[ 1 - \left( \frac{u}{\sqrt{\alpha}} \right)^2 \right] + \frac{\gamma \left[ 1 - \left( \frac{1}{\sqrt{\alpha}} \right) \ln(1 + \frac{u}{\sqrt{\alpha}}) + \left( 1 - \frac{u}{\sqrt{\alpha}} \right) \ln(1 - \frac{u}{\sqrt{\alpha}}) \right] - 2\ln(2)}{2\ln(2)} \right\},$$  \hspace{1cm} (31)

with $u (-\sqrt{\alpha} < u < \sqrt{\alpha})$ given by:

$$u = \frac{e - e_o}{\bar{\epsilon}}.$$  \hspace{1cm} (32)

This is a linear combination -weighted by the parameter $\gamma$- of the parabolic configurational entropy typical of the gaussian model and a term that depends on the logarithm of the energy. Here we want to describe in detail the properties of this model for the specific case $\gamma = 1$, i.e. of a model that is totally "logarithmic". The logarithmic model is essentially a binomial distribution, i.e. model for the thermodynamics of a gas of binary
excitations. It has been used to model the thermodynamics of supercooled liquids and the T-dependence of the inherent structure energy. Obviously, the logarithmic term in Eq. (33) becomes dominant in the low-T/low-\((e - e_K)\) region, therefore the model discussed in this section can be thought as an approximation of the Debenedetti, Stillinger and Shell model valid in the low T limit. It is, however, interesting to study such a model in the whole energy range. Indeed, as we will see below, a visual inspection of the function \(\Sigma(e)\) indicates that this model and the gaussian model represent very similar "landscapes", i.e. very similar distribution of the minima energy. Thus, we define the "logarithmic" landscape as:

\[
\Sigma(e) = Nk_B \alpha \times \left[ 1 - \frac{(1 + \frac{u}{\sqrt{\alpha}}) \ln(1 + \frac{u}{\sqrt{\alpha}}) + (1 - \frac{u}{\sqrt{\alpha}}) \ln(1 - \frac{u}{\sqrt{\alpha}})}{2 \ln(2)} \right]
\]  

(33)

This expression for the configurational entropy has the properties to vanish at \(u = \pm \sqrt{\alpha}\), therefore the Kauzmann energy results to be at \(u = -\sqrt{\alpha}\) or explicitly \(e_K = e_o - \sqrt{\alpha}\). At this energy, the derivative of \(\Sigma(e)\) shows a logarithmic divergence, thus implying that the Kauzmann temperature must vanish. Similarly to the gaussian model, the parameter \(e_o\) is the energy of the "top of the landscape" and \(\alpha\) represents the maximum of \(\Sigma(e)/Nk_B\). Using Eq. (32) and the expression for \(e_K\), Eq. (33) can be explicitly written in terms of the reduced energy measured with respect to the Kauzmann energy \(v = (e - e_K)/\bar{\epsilon}\) as:

\[
\Sigma(e) = Nk_B \alpha \left[ 1 - \frac{\frac{u}{\sqrt{\alpha}} \ln(\frac{u}{\sqrt{\alpha}}) + (2 - \frac{u}{\sqrt{\alpha}}) \ln(2 - \frac{u}{\sqrt{\alpha}})}{2 \ln(2)} \right]
\]

(34)

We can now follow the same route used in the discussion of the gaussian model. Via Eq. (14) with straightforward algebra, we obtain the temperature dependence of the energy of the minima:

\[
e(T) - e_o = -\bar{\epsilon} \sqrt{\alpha} \tanh \left[ \frac{2 \ln(2) \bar{\epsilon}}{\sqrt{\alpha} k_B T} \right]
\]

(35)

and inserting this expression in Eq. (33) the temperature dependence of the configurational entropy is promptly derived:

\[
\Sigma(T) = Nk_B \alpha \left\{ \frac{1}{\ln(2)} \ln \left[ 2 \cosh \left( \frac{\ln(2) \bar{\epsilon}}{\sqrt{\alpha} k_B T} \right) \right] - \frac{\bar{\epsilon}}{\sqrt{\alpha} k_B T} \tanh \left( \frac{\ln(2) \bar{\epsilon}}{\sqrt{\alpha} k_B T} \right) \right\}
\]

(36)

As a consequence of the infinite value of \(\Sigma(e)/de\) at \(e_K\), this function does vanish only at \(T = 0\), i.e. for this model \(T_K = 0\). It is convenient, for sake of compactness, to define a typical temperature which -in analogy with \(T_K\) in the gaussian and hyperbolic models- could be used to scale the temperatures in the logarithmic model. We arbitrarily introduce the quantity:

\[
T_K^* = \frac{1}{3} \ln(2) \frac{\bar{\epsilon}}{k_B \sqrt{\alpha}}
\]

(37)

whose value is very close to the "apparent" Kauzmann temperature that would have been identified by extrapolating Eq. (33) towards zero using only information on \(\Sigma(T)\) at "high" temperature, similarly to what is done experimentally. In other words, the logarithmic model predicts a temperature dependence of the configurational entropy that -around the inflection region- can be approximated by a straight line that goes to zero at \(k_B T_K \sqrt{\alpha}/\bar{\epsilon} \approx 0.23 \approx (\ln(2))/3\). Having introduced the "apparent" Kauzmann temperature for the logarithmic model, we can write Eq.s (35) and (36) as:

\[
e(T) - e_o = \frac{3}{\ln(2)} \alpha k_B T_K^* \tanh \left( \frac{3T_K^*}{T} \right)
\]

(38)

\[
\Sigma(T) = \frac{Nk_B \alpha}{\ln(2)} \left\{ \ln \left[ 2 \cosh \left( \frac{3T_K^*}{T} \right) \right] - \frac{3T_K^*}{T} \tanh \left( \frac{3T_K^*}{T} \right) \right\}
\]

Once the explicit \(T\) dependence of \(\Sigma(T)\) is known, both the fragility \(m_s\), definite in Eq. (10), and the \(T\) dependence of the viscosity (from the Adam-Gibbs equation) can be worked out. The two expressions reads:

\[
m_s = 1 + \left( \frac{3T_K^*}{T_g} \right)^2 \left\{ \cosh \left( \frac{3T_K^*}{T_g} \right) \ln \left[ 2 \cosh \left( \frac{3T_K^*}{T_g} \right) \right] - \left( \frac{3T_K^*}{T_g} \right) \cosh \left( \frac{3T_K^*}{T_g} \right) \sinh \left( \frac{3T_K^*}{T_g} \right) \right\}^{-1}
\]

(39)
\[ \alpha - u^2 \]  
\[ \alpha [1 - \exp (-2u)] \]  
\[ \alpha \left[ 1 - \frac{1}{2 \ln(2)} \left[ (1 + \frac{u}{\sqrt{\alpha}}) \ln(1 + \frac{u}{\sqrt{\alpha}}) + (1 - \frac{u}{\sqrt{\alpha}}) \ln(1 - \frac{u}{\sqrt{\alpha}}) \right] \right] \]

\[ \Sigma(e)/Nk_B \{ \]
\[ -v^2 + 2\sqrt{\alpha} v \]  
\[ \alpha [1 - \exp (-2v)] \]  
\[ \alpha \left[ 1 - \frac{1}{2 \ln(2)} \left[ (1 + \frac{u}{\sqrt{\alpha}}) \ln(1 + \frac{u}{\sqrt{\alpha}}) + (1 - \frac{u}{\sqrt{\alpha}}) \ln(1 - \frac{u}{\sqrt{\alpha}}) \right] \right] \]

\[ e_K \]  
\[ e_o - \bar{\epsilon} \sqrt{\alpha} \]  
\[ e_o - \bar{\epsilon} \sqrt{\alpha} \]

\[ k_B T_K \]  
\[ \frac{\bar{\epsilon}}{\sqrt{\alpha}} \]  
\[ \frac{\ln(2) \sqrt{\alpha}}{\sqrt{\bar{\epsilon}}} \]

\[ e(T) - e_o \]  
\[ -2\alpha k_B T_K \left( \frac{T}{T_\infty} \right) \]  
\[ \alpha k_B T_K \ln \left( \frac{T}{T_\infty} \right) \]  
\[ \frac{3}{\ln(2)} \alpha k_B T_K \tanh \left( \frac{3 T_K}{T} \right) \]

\[ e(T) - e_K \]  
\[ 2\alpha k_B T_K \left( 1 - \frac{T}{T_\infty} \right) \]  
\[ \alpha k_B T_K \ln \left( \frac{T}{T_\infty} \right) \]  
\[ \frac{3}{\ln(2)} \alpha k_B T_K \left[ 1 - \tanh \left( \frac{3 T_K}{T} \right) \right] \]

\[ \Sigma(T)/Nk_B \]  
\[ \alpha \left[ 1 - \left( \frac{T}{T_\infty} \right)^2 \right] \]  
\[ \alpha \left[ 1 - \left( \frac{T}{T_\infty} \right) \right] \]  
\[ \frac{\alpha}{\ln(2)} \left\{ \ln \left[ 2 \cosh \left( \frac{3 T_K}{T} \right) \right] - \frac{3 T_K}{T} \tanh \left( \frac{3 T_K}{T} \right) \right\} \]

\[ m_o \]  
\[ \frac{T_o^2 + T_K^2}{T_o^2 - T_K^2} \]  
\[ \frac{T_o}{T_o - T_K} \]  
\[ 1 + w^2 \left\{ \cosh^2 (w) \ln \left[ 2 \cosh (w) \right] - w \cosh (w) \sinh (w) \right\}^{-1} \]

\[ \ln \left( \eta(T)/\eta_\infty \right) \]  
\[ \frac{D T_K}{T - T_K} \]  
\[ \frac{D T_K}{T - T_K} \]  
\[ \left\{ \frac{\ln(2) D}{3 T_K} \left[ 2 \cosh \left( \frac{3 T_K}{T} \right) \right] - \frac{3 T_K}{T} \tanh \left( \frac{3 T_K}{T} \right) \right\}^{-1} \]

| gaussian model | hyperbolic model | logarithmic model |
|----------------|-----------------|-----------------|
| \[ \alpha - u^2 \] | \[ \alpha [1 - \exp (-2u)] \] | \[ \alpha \left[ 1 - \frac{1}{2 \ln(2)} \left[ (1 + \frac{u}{\sqrt{\alpha}}) \ln(1 + \frac{u}{\sqrt{\alpha}}) + (1 - \frac{u}{\sqrt{\alpha}}) \ln(1 - \frac{u}{\sqrt{\alpha}}) \right] \right] \] |

TABLE I: Summary of the main relations relating the relevant quantities (left column) for the three configurational entropy models introduced before. The relation that define the model is reported in box. The variable \( u \) is defined as the reduced energy measured with respect to \( e_o \): \( u = (e - e_o)/\bar{\epsilon} \), while \( v \) is that measured starting from the Kauzmann energy: \( v = (e - e_K)/\bar{\epsilon} \). The variable \( w \) is a shortcut for \( 3T_K/T_o \). In the case of the logarithmic model, \( T_K \) is used (see Eq. 37) in place of the Kauzmann temperature.

\[ \eta(T) = \eta_\infty \exp \left\{ \frac{1}{3} \ln(D) \left( \frac{3 T_K}{T_o} \right) \left\{ \ln \left[ 2 \cosh \left( \frac{3 T_K}{T} \right) \right] \right\} - \left( \frac{3 T_K}{T_o} \right) \tanh \left( \frac{3 T_K}{T} \right) \right\}^{-1} \]

\( \eta(T) = \eta_\infty \exp \left\{ \frac{1}{3} \ln(D) \left( \frac{3 T_K}{T_o} \right) \left\{ \ln \left[ 2 \cosh \left( \frac{3 T_K}{T} \right) \right] \right\} - \left( \frac{3 T_K}{T_o} \right) \tanh \left( \frac{3 T_K}{T} \right) \right\}^{-1} \]

Summary of models

In Table I, we summarize the expressions derived in the framework of the three model examined before for different quantities. These quantities are:

i) and ii) the configurational entropy as a function of \( e \), in this case we explicitly report \( \Sigma(e) \) as a function of the variables \( u = (e - e_o)/\bar{\epsilon} \) and \( v = (e - e_K)/\bar{\epsilon} \) to emphasize that the zero of the energy is irrelevant and that \( \bar{\epsilon} \) only acts as an energy scale.

iii) The explicit expression of the Kauzmann energy in term of \( e_o \), \( \alpha \) and \( \bar{\epsilon} \).

iv) and v) The relations used to eliminate \( \bar{\epsilon} \) in favor of \( T_K \) (or \( T_K \) in the case of the logarithmic model).

vi) and vii) The temperature dependence of the inherent structures energy, reported in terms of \( T_K \).

viii) The temperature dependence of the configurational entropy, now reported in term of \( T_K \).

ix) The expression for the fragility reported in terms of the thermal parameters.

x) Finally, we report the temperature dependence of the viscosity resulting from the application of the model. In the last expression the parameter \( D \) is:

\[ D = \mathcal{E}/(\alpha Nk_B T_K) \].
FIG. 2: Plot of the temperature dependence of the configurational entropy for three models: gaussian (full line), hyperbolic (dashed line) and logarithmic (dot-dashed line). The reduced entropy $\Sigma(T)/Nk_B$ further normalized to $\alpha$ is plotted as a function of $T/T_K$. In the case of the logarithmic model $T^*_K$ defined in Eq. 37 is used in substitution of $T_K$.

FIG. 3: Similarly to Fig. 2 the temperature dependence of the configurational entropy for three models (gaussian (full line), hyperbolic (dashed line) and logarithmic (dot-dashed line)) is plotted as a function of $T_K/T$. In the case of the logarithmic model $T^*_K$ defined in Eq. 37 is used in substitution of $T_K$.

In Fig. 4 we report the temperature dependence of the energy elevation (normalized to the factor $\alpha k_B T_K$) with respect to $e_K$ of the minima of the PEL visited at equilibrium for the three examined models: gaussian (full line), hyperbolic (dashed line) and logarithmic (dot-dashed line). The hyperbolic model shows a non physical continued rise of $e(T)$ at increasing $T$.

FIG. 4: Plot of the temperature dependence of the energy elevation for three models: gaussian (full line), hyperbolic (dashed line) and logarithmic (dot-dashed line). The energy elevation $e-e_K$, normalized to $k_B T_K$, and further normalized to $\alpha$, is plotted as a function of $T/T_K$. In the case of the logarithmic model $T^*_K$ defined in Eq. 37 is used in substitution of $T_K$.

Finally, in Fig. 5 we report in Arrhenius scale the temperature dependence of the viscosity for the three examined models: gaussian (full line), hyperbolic (dashed line) and logarithmic (dot-dashed line).

Gaussian models with non-constant vibrational entropy

All the discussion in the previous sections was based on the assumption that the vibrational entropy associated to a given basin is independent from the energy elevation of the minimum of the basin itself. These assumption lead to the simplified microcanonical definition of temperature reported in Eq. 14. Following recent experimental [37] and numerical [26, 42] evidences indicating a vibrational entropy that actually depends on the energy of the minima, in the present section we relax the previous assumption, and, for the specific case of the gaussian model, we develop the calculation in the case of an explicit dependence of the vibrational entropy, $S_v$, on $e$. In particular, taking advantage of the outcome of recent molecular dynamics calculations, we develop $S_v(e)$ in series of $e-e_K$ and retain only the first order term, an approximation certainly valid for low enough tempera-
thus, substituting this expression in Eq. (43)

\[ \Sigma(T) = k_B N \alpha \left[ 1 - \left( \frac{T_K}{T_v - T_K} \right)^2 \left( \frac{T_v}{T} - 1 \right)^2 \right] \]  

(47)

Through the configurational entropy, we can apply Eq. (40) to find an expression for the fragility:

\[ m_g = \left( \frac{T_g^2 + T_v^2}{T_v^2} - 2 T_g T_K (T_v/T_g) \right) \left( \frac{T_v}{T} - T_K \right)^2 \]  

(48)

In this expression, besides \( T_g \) -the parameter that embodies our choice of the value of viscosity that define the glass transition temperature- there are the two system-dependent parameter \( T_K \) (a way to express \( \bar{\varepsilon} \)) and \( T_v \). Finally the temperature dependence of the viscosity turns out to be controlled by the law:

\[ \eta(T) = \eta_\infty \exp \left( \frac{D T_K}{T - T_K} \left( \frac{T_v}{T} - T_K \right)^2 \right) \left( \frac{T_v}{T} \right)^{2} \]  

(49)

with, as before, \( D = -E/(\alpha N k_B T_K) \).

Similarly to Fig. 4 in Fig. 5 we report the temperature dependence of the configurational entropy of the gaussian model with energy dependent vibrational entropy as a function of \( T_K/T \) for different values of \( T_v/T_K \) (reported in the figure) and compared with the similar quantity for the gaussian and the hyperbolic models.

\[ \Sigma(T) = k_B N \left[ \alpha - \frac{\tilde{\varepsilon}^2}{4} \left( \frac{1}{k_B T_v} - \frac{1}{k_B T_v} \right)^2 \right] \]  

(45)

We can now eliminate \( \tilde{\varepsilon} \) by introducing the Kauzmann temperature defined by \( \Sigma(T_K) = 0 \):

\[ \tilde{\varepsilon} = 2 \sqrt{\alpha} k_B T_K \left( \frac{T_v}{T_v - T_K} \right) \]  

(46)
FRAGILITY AND NUMBER OF STATES

In the following sections we will discuss the possibility to predict the fragility of a system from the knowledge of the parameters characterizing the distribution of the minima of the PEL. First, we analyze the recent works that have attempted to relate the fragility to the "number of states". Secondly we will see how given a fixed configurational entropy model one can obtain the whole range of fragilities, thus demonstrating that, in order to assess the fragility of a system, some additional information is needed.

Speedy’s expression of fragility

In 1999 Speedy \[26\] -working in the framework of the gaussian model and assuming the validity of the Adam-Gibbs relation- choose to express \( m_s \) ("\( F \)" in his language) in term of \( \alpha \) and \( \Sigma(T_g) \) ("\( \Delta_1 s(T_g) \)" in Ref. \[25\]). With these variables, Eq. \[20\] becomes:

\[
m_s = \frac{2\alpha}{\Sigma(T_g)/Nk_B} - 1. \tag{50}
\]

Speedy used this relation to state that "...this quantifies the Angell observation that fragile liquids sample more basins in configuration space than strong liquids". Actually, Eq. \[50\] does not help much in establishing whether or not the reported Angell observation is correct. Indeed the proportionality between \( m_s \) and \( \alpha \) holds only if one neglects the possibility that \( \Sigma(T_g) \), a system-dependent quantity, depend on \( \alpha \). In principle its implicit dependence on \( \alpha \) can also reverse the fragility-number of states relation.

Sastry’s expression of fragility

More recently another expression for the fragility in term of the PEL features was derived by Sastry \[26\]. Also in this case the gaussian model and the Adam-Gibbs equation are at the basis of the theory. However, Sastry does not use Eq. \[10\] to obtain the fragility. He assumed i) the validity of the VTF law, so to relate (compare Eq. \[9\] and \[3\]) the configurational entropy to the coefficient \( D \), which, as discussed before, is an index of kinetic fragility (actually, Sastry reports his expression for the fragility \( K = 1/D \)), and ii) the coincidence of \( T_o \) with \( T_K \). The Sastry expression takes also into account the possible energy-depth dependence of the basin vibrational free energy. In order to compare the expression reported in Ref. \[26\] with Eqs. \[20\] and \[50\] however, we can put the quantity \( \delta S \) (in Sastry’s notation) equal to zero. The Sastry expression becomes (with the change of notation from \( \sigma \) to \( \bar{\sigma} \)):

\[
K = \frac{\bar{\epsilon} \sqrt{\alpha}}{2\bar{\epsilon}} \left( 1 + \frac{T_K}{T_g} \right). \tag{51}
\]

Here "\( T_g \)" is the MD glass transition temperatures. In Eq. \[51\] we have explicitly included the Adam-Gibbs constant \( \bar{\epsilon} \) which was implicitly assumed constant and landscape independent in Ref. \[26\] (see also \[54\]).

After the conversion from \( K \) to \( m_s \), using Eq. \[6\] we have:

\[
m_s = 17 \ln(10) \frac{\bar{\epsilon} \sqrt{\alpha}}{2\bar{\epsilon}} \left( 1 + \frac{T_K}{T_g} \right) + 1 \tag{52}
\]

Similarly to Eq. \[50\] also this equation cannot be used to predict the \( \alpha \) dependence of the fragility. Indeed, \( \alpha \)}
appears here explicitly but also implicitly, via the system-dependent quantities \( \tilde{\epsilon} \) and \( T_K \) (see Table I). Finally, we want to stress that the approach followed in the derivation of the previous expression of the fragility is intrinsically inconsistent. Indeed, as previously pointed out, the gaussian landscape (i), the VTF law (ii) and the Adam-Gibbs relation (iii) are not mutually consistent and, as also noticed by Sastry [26], the hypothesis i)-iii) can only be consistent if one uses a low temperature expansion of \( \Sigma(T) \).

Can the fragility be derived entirely from the configurational entropy?

We aim now to prove with an example that, in general, the configurational entropy alone is not sufficient to determine the fragility of a system. We will use the gaussian model for the configurational entropy and, with the help of Eq. 21, we will set-up an “Angell plot”. We could have selected any other landscape model, reaching the same conclusion. Let’s suppose to have an hypothetical system, fully defined by a gaussian landscape with a given value of the relevant parameters \( \alpha \), \( \epsilon \) and \( e_o \). The temperature dependence of the viscosity in this model is reported in Eq. 21, by definition

\[
\ln \left( \frac{\eta(T)}{\eta_\infty} \right) = \frac{DT}{T - T_K}.
\]

We can now eliminate \( T_K \) from this equation in favor of \( T_g \) using Eq. 55 (\( T_K = T_g / \gamma(D) \)) to get:

\[
y(T) = \left( \frac{T_g}{T} \right) \frac{\gamma(D)^2 - 1}{\gamma(D)^2 - \left( \frac{T_g}{T} \right)^2}.
\]

\( D = 2\mathcal{E}/(\alpha N k_B T_K) \) that, in turn, embodies the information on the "number of states" but also from quantities distinct from the statistic of the minima (specifically from the parameter \( \mathcal{E} \)). We want now to plot the re-scaled logarithmic viscosity \( y(T) = [\ln(\eta(T)/\eta_\infty)]/[\ln(\eta(T_g)/\eta_\infty)] \) as a function of \( T_g/T \). The quantity \( y(T) \), by definition of \( T_g \), turns out to be equal to \( y(T) = [\log(\eta(T)/\eta_\infty)]/17 \), or, by using the expression for \( T_g(T) \) reported in Eq. 21 to:

\[
y(T) = \frac{D}{17 \ln(10)} \frac{T}{T - T_K} - \frac{T}{T + T_K}.
\]
In Fig. 8 we have reported the quantity $y(T)$ of Eq. 57 vs. $T_g/T$, i.e. we have made an Angell plot, for different values of the parameter $E$ at fixed $\alpha$ and $\bar{\epsilon}$. The fragilities $m_s$ are the slopes of these curves at the upper right corner of the plot. What is remarkable here is that, by varying the quantity $E$ entering in the numerator of the exponent in the Adam-Gibbs relation (Eq.[9]) at fixed configurational entropy, we can span the whole range of fragilities. In other words, for a given (gaussian in the present example) landscape, with well defined statistical properties (fixed $\alpha$ and $\bar{\epsilon}$), we can have a strong system (large $E$) as well as a fragile one (small $E$). Therefore, we conclude this section with the statement that in principle -whenever the Adam Gibbs relation represents a good approximation of the relation between transport properties and configurational entropy- the knowledge of the configurational entropy alone would be not sufficient to define the fragility of a system. This statement, and the role of the effective barrier height in determining the fragility of a glass has been already discussed in literature (see e.g. Ref. 57). The previous conclusion does not imply that the fragility cannot be derived from the landscape properties: indeed, it is possible, and actually most likely, that the quantity $E$ could be derived from other features of the PEL than the minima distribution, as, for example the minimum-to-minimum barrier heights. Future studies must focus on the relation between $E$ and the PEL properties and on the physical range of values of $E$.

**Strong-to-fragile transition**

In the previous section we have shown that, on a general ground, a simple gaussian landscape with fixed statistical properties could be shared by the whole class of known systems; they would simply differ in the value of $E$ that, in turn, induces a different value of $T_g/T_K$, thus a different fragility. In this scheme a fragile system -having $T_g$ close to $T_K$ (as deduced from Eq. 20)- visits that part of the landscape where $\Sigma(e)$ is strongly dependent, thus (see Eq. 10) pushing $m_s$ up. On the contrary, a strong system has $T_g$ far away from $T_K$, and the system is confined to visit the region where $\Sigma(e)$ is almost flat. In other words, if all the system shared the same landscape, due to the difference in the parameter $E$, a strong system (large $E$) would visit the "top-of- the-landscape", while a fragile system (small $E$) would be allowed to go down in energy. If this scenario were correct, we would expect that real systems verify Eq. 20 (or 30, or 39). In Fig. 9 we report, for those systems where all the three quantities $T_g$, $T_K$ and $m_s$ are known (see Table III), the fragility $m_s$ as a function of $T_g/T_K$ (symbols). Also shown in the same figure are the predictions of Eq.s 20 30 39 (lines). Few points must be underlined: i) there is a rather good general agreement, but the single systems does not strictly verifies none of the three predictions. This can be due to the existence of landscapes different from the three simple cases discussed at the beginning of this chapter, or, most likely, to the presence of a finite value for $T_w$. Indeed, recent molecular simulations of model liquids [45] clearly show such a phenomenology, indicating a non negligible energy dependence of the vibrational entropy. ii) The differences among Eq. 20 and 30 are so small, that the experimental data do not allow to discriminate among these two different landscape models, while the (pure) logarithmic model seems to be definitely unacceptable. Most likely, a gaussian model with a small logarithmic correction would be still acceptable. iii) Among the systems represented in Fig. 9 the lowest fragility is $\approx 35$, i.e. the strong systems are absent (for these systems a reliable estimation of $T_K$ does not exist), and this does not allow to firmly establish the general validity of one of the three model, and, more generally, of the idea presented before that strong systems and fragile systems are characterized by a common configurational entropy and a different elevation in the PEL.

Of course, we are not stating that the depicted behaviour is the actual one. Different systems have different value of $\alpha$ and may even not be described by a common landscape model. A typical example, that it is worth to discuss here, is the case of silica. As shown by Horbach and Kob 58, vitreous silica (as described by the BKS potential model 59) show strong $T$-dependence of the fragility. More specifically, $\nu$-SiO$_2$, which is a well known strong system close to the glass transition temperature, turns toward a more fragile behaviour on increasing $T$. This phenomenon, called "strong-to-fragile" transition, first proposed for the case of water [60], has been observed in simulations of water [61] and (simulated) berillium flu-
TABLE III: Summary of the quantity relevant to test Eq. (20) \( (T_g, T_K, m_S) \) for those systems where the three quantity are all known. The last column reports the references where the data has been found. In those case where more than one value of the parameters are known, we have reported here the average value. The first of the two references refers to the couple \( (T_g, T_K) \) and the second to \( m_S \).

| Compound               | \( T_g \) | \( T_K \) | \( m_S \) | Ref. |
|------------------------|-----------|-----------|-----------|------|
| 2-methylpentane        | 80.5      | 58        | 58        | [24], [24] |
| butyronitrile          | 100       | 81.2      | 47        | [24], [24] |
| ethanol                | 92.5      | 71        | 55        | [24], [55] |
| n-propanol             | 102.5     | 73        | 36.5      | [24], [24] |
| toluene                | 126       | 96        | 59        | [24], [55] |
| 1-2 propan diol        | 172       | 127       | 52        | [24], [24] |
| glycerol               | 190       | 135       | 53        | [24], [24] |
| triphenyl phosphate    | 205       | 166       | 81        | [24], [24] |
| orthoterphenyl         | 244       | 200       | 81        | [24], [24] |
| m-toluidine            | 187       | 154       | 79        | [24], [24] |
| propylene carbonate    | 156       | 127       | 104       | [24], [24] |
| sorbitol               | 266       | 226       | 93        | [24], [24] |
| selenium               | 307       | 240       | 87        | [24], [24] |
| ZnCl\(_2\)             | 380       | 250       | 30        | [24], [55] |
| As\(_2\)S\(_3\)        | 455       | 265       | 36        | [24], [55] |
| CaAl\(_2\)Si\(_2\)O\(_8\) | 1118    | 815       | 53        | [24], [55] |
| Propilen Glycol        | 167       | 127       | 52        | [27], [27] |
| 3-Methyl pentane       | 77        | 58.4      | 36        | [27], [27] |
| 3-Bromopentane         | 108       | 82.5      | 53        | [27], [27] |
| 2-methyltetrahydrofuran| 91        | 69.3      | 65        | [27], [27] |

oride[62]. It is obvious that the fragile-to-strong transition cannot be framed within the possibility described in the first paragraph of this section.

In a recent simulations work, Saika-Voivod, Sciortino and Poole[63] have shown that the configurational entropy for liquid silica -as derived from a MD simulation based on the BKS interaction potential model- is far from being “gaussian”. More specifically, they found that \( \Sigma(T) \) -at low \( T \)- shows a tendency towards a positive curvature and does not seem to extrapolate to zero entropy at a finite temperature. This behavior is shared by the logarithmic model (or by a combination of the logarithmic and gaussian models, as proposed in Ref. [49]) for \( \Sigma(e) \). This model predicts an infinite slope of \( \Sigma(e) \) at \( e_K \) alone is not sufficient to guarantee the existence of a strong-to-fragile transition. What is actually sufficient (necessary?) for a strong to fragile transition -i.e. have a maximum in the \( m_S \) vs. \( T_g/T_K \) function- is that the configurational entropy -as a function of \( T \)- had a non-zero limit for \( T \to 0 \). This can be understood looking at Eq. (10). It is clear that a fragile system is characterized by a large value of \( \Sigma'(T) \) (fragile systems explore the ”steep” part of the PEL), while a strong system will have a small value of \( \Sigma'(T) \), but also a non zero \( \Sigma(T) \). This certainly happens at the ”top of the landscape”, but could also happen at low \( T \) if \( \Sigma(0) \neq 0 \) (in the logarithmic model, at low \( T \), \( \Sigma'(T) \to 0 \), but the same does \( \Sigma(T) \) and the resulting fragility increases continuously). Thus, a strong-to-fragile transition could take place only if the landscape of the systems allows for a finite number of states at zero temperature, i.e. for a (exponentially large with \( N \)) degenerate fundamental state. The existence of such a degeneracy for system with short range interaction (non mean field systems) poses toward a \textit{decrease} of the fragility on increasing temperature (see Fig. 10). A behavior opposite to what observed in simulated vitreous silica. It is therefore clear that an infinite slope of \( \Sigma(e) \) at \( e_K \) alone is not sufficient to guarantee the existence of a strong-to-fragile transition.

The logarithmic model, however, similarly to the other models presented before, is not capable to catch the physics of the strong-to-fragile transition. Indeed, the fragility expressions for all the examined models (Eq.s 20, 30, 39) show a \textit{monotonic} \( T \) dependence, whith a tendency...
FIG. 9: Experimental values of the kinetic fragility $m_A$ plotted as a function of the ratio $T_g/T_K$ for those systems where the three quantities ($m_A$, $T_g$, and $T_K$) are available. The input data are reported in Table III. For those systems where more than one determination of the parameters is known, we have reported in the plot the average value together with an "error" bar that indicates the whole dispersion.

several problems (see the discussion in Ref. [49]), and is certainly calling for further investigation.

FIG. 10: Temperature dependence of the fragility for the three examined models: gaussian (full line), hyperbolic (dashed line) and logarithmic(dot-dashed line). The quantity $m_S$ is reported as a function of $T_g/T_K$.

DISCUSSION AND CONCLUSION

In conclusion, in this paper we have first summarized the main definition of fragility, then we have recalled and studied different models for the configurational entropies present in the literature. Using the Adam-Gibbs relation to link the dynamics of a glass forming system to its configurational entropy, we have reported the explicit expressions for different quantities, among which the fragility. From the reported relation, it is clear that in general the fragility cannot be derived by the knowledge of the configurational entropy. More specifically, given a fixed "landscape", different system fragility can be mimicked by varying the parameter $\Sigma$ entering in the numerator of the Adam-Gibbs equation. On a general ground, the fragility of a system depends on the ratio $\Sigma/\alpha N k_B T_K$.

The fact that the whole range of fragility can be derived from a given PEL model (e.g. the gaussian model) with the same statistical properties seems an interesting possibility. If this was the case, the strong glass forming materials would be characterized by a large value of $\Sigma$ and would explore the "top-of-the-landscape", while the most fragile ones would have small $\Sigma$ and would visit the states around the inflection point of $\Sigma(T)$. Obviously other possibilities exist, as for example that all the systems were characterized by the same $\Sigma$, and in this case strong glass would have a small number of states (small $\alpha$), at variance to the fragile systems with more states (large $\alpha$).

A further scenario can be hypothesized, that would also explain the existence of a strong-to-fragile transition: in this case the strong systems would explore the bottom of a landscape characterized by a non-vanishing zero point entropy. This is an interesting possibility that deserve deeper investigation.

Overall, the present discussion, which heavily build on the validity of the Adam and Gibbs relation, indicates that in principle at least two possible classes of strong glass forming materials can actually exist. On one side we have those systems that -close to $T_g$- visit state at the top of the landscape and have a "regular" (gaussian-like) configurational entropy (let’s call these systems as class A strong glass forming materials). On the other side we find the -let’s say- class B strong liquids, that visit minima deep in the PEL, but with an exponentially large degeneracy of the fundamental state. The answer to the question whether class A and/or B strong systems actually exist requires further investigations.

As a final comment, we would like to recall that fragility is often measured at constant pressure, while all the configurational entropy based models -as those presented here- are built on the assumption of a well defined $\Sigma(e)$ function, i.e. they assume constant density. The relationship between constant density and constant pressure fragilities is one of the topic under discussion at the present time. As an example, in the case of soft sphere systems it has been shown that $\Sigma(T)$ along isochoric and isobaric are very close one to each other. Similarly, in a very recent work, Tarjus and coworkers show that in alcohols the change in density only slightly affects the fragility, thus indicating that under the experimentally accessible density changes the landscape suffers only minor modifications. For other systems, on the contrary, it has been observed a large deviation ($\approx 40\%$)
between constant density and constant pressure fragilities [40]. This ongoing discussions, however, does not affect the conclusions of the present work since all the formalism could have been based on the enthalpy landscape, instead of energy landscape, without any changes in the results.

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Note that Eq. 8 in Ref. [26] defines a fragility index with the dimension of energy. In the caption of Fig. 1, Sastry clarifies that in order to have a dimensionless fragility index a dimensional quantity is needed in going from $T_S$ which is a dimensional quantity and fragility which is dimensionless. In the absence of a good way to calculate $E$, Sastry choose the Lennard Jones energy scale $\epsilon_{AA}$, finding support for such a choice in the numerical data. This choice leads to the approximation $K = \frac{\epsilon_{AA}}{2\pi} \left( 1 + \frac{T_k}{T} \right)$, to be compared with the exact expression $K = \frac{\epsilon_{AA}}{2\pi} \left( 1 + \frac{T_k}{T} \right)$, reported in Eq. 53.

The existing correlation between thermodynamic ($m_T$) and kinetic ($m_s$) fragilities - as experimentally observed in Ref. 32 - is NOT in contradiction with the statement that $\Sigma(T)$ alone is not sufficient to determine fragility. Indeed, the experimentally observed correlation between $m_T$ and $m_s$ (discussed in Eq. 11 of the manuscript) can be derived — beyond assuming the proportionality between configurational and excess entropy — from i) the definition of $m_T$ (Eq. 7), ii) the definition of $m_s$ (Eq. 2), iii) the AG relation.

We stress that Eq. 11 is independent from whether or not the fragility could be derived from $\Sigma(T)$ only. Note that, as shown in Eq. 7, the evaluation of $m_T$ requires the knowledge of two thermodynamic quantities (the excess entropy and the T-derivative of it) but also the knowledge of one dynamical quantity ($T_g$). The presence of $T_g$ in the definition of $m_T$ highlight the need of dynamical information in the evaluation of the fragility.

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