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JOURNAL OF CHEMICAL PHYSICS VOLUME 120, NUMBER 22 8 JUNE 2004

Landscapes and fragilities

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(Received 23 January 2004; accepted 10 March 2004)

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. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1736628]

I. INTRODUCTION

Soon after the introduction of the concept of the "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[3] PEL local minima (inherent structures), Ω_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 Ω_N function, or, more specifically, to the steepness of the N dependence of this quantity. From general arguments, in a monocomponent collection of a large number, N of units (atoms, molecules,...), it can be shown that $\Omega_N \sim \exp(\alpha N)$. Similarly, it holds that $\Omega_N(E) \sim \exp(\Sigma(e)/k_B)$. 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 α ($\alpha = \max_e\{\Sigma(e)\}/Nk_B$) is a measure of the total number of "inherent structures" (individual minima of the potential energy hypersurface). In comparing the behavior of different glass-forming systems, particular emphasis is placed in the relation existing between α 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 (τ_α) increases with decreasing temperature on approaching the glass transition temperature, T_g, defined as the temperature where τ_α becomes equal to 100 s. "Strong" systems (low values of fragility) show a "weak" T dependence of $\tau_\alpha(T)$, that 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 Δ). The relaxation time is a quantity that is rather difficult to access, in particular, when the value of τ_α is large, and, moreover, it seems also to be technique dependent. For these reasons, in nonpolymeric liquids, the fragility is usually defined through the T dependence of the shear viscosity, η.[5] 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_∞ is the infinite frequency shear modulus of the liquid), and recalling that G_∞ 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 [$D = k_BT/(6\pi r\eta)$, r being the effective hydrodynamic radius], it is the *mobility* μ ($=D/T$) 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 η, 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,[6,7] (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

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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.[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.*[18] proposed to associate two indexes to every glassformer. The first index (fragile/nonfragile) measures how much the viscosity is Arrhenius-type 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. 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[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. 21. There the landscapes of strong liquids were supposed to have a ''uniform'' roughness, while a two-length scale arrangement of the minima—with the introduction of the *meta basins*, a concept that has been recently revitalized by Doliwa and Heuer[22]—was expected to characterize the PEL of fragile liquids. In 1995, Angell,[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. 24 and by Debenedetti and Stillinger,[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

$$\text{strong systems} \Leftrightarrow \text{small } \alpha,$$

$$\text{fragile system} \Leftrightarrow \text{large } \alpha.$$

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,[25] who derived a direct proportionality between kinetic fragility and α. This relation has been then criticized by Sastry,[26] who—again using the Gaussian model to fit his molecular dynamics simulation of the Kob–Andersen Lennard-Jones Binary Mixture (BMLJ) at different densities—reached the conclusion of a proportionality between fragility and the square root of α.

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 a 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 α dependence of the fragility for the examined landscapes. Finally, we emphasize that landscapes with the same statistical properties (i.e., the same total number of basins, the 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.

II. FRAGILITIES

As discussed in the Introduction, and following Angell,[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 assess 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.

A. Kinetic fragility: Local definitions

The first definition, let us call it ''Angell's kinetic fragility,'' m_A, is

$$m_A \doteq \left. \frac{d \log(\eta(T)/\eta_\infty)}{d(T_g/T)} \right|_{T=T_g}. \tag{1}$$

Here η_∞ 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 $\eta_\infty \cong 10^{-4}$ Poise, this quantity is *conventionally* fixed to this value. Accordingly, an ideal strong glass (strictly Arrhenius behavior) would have $m_A \cong 17$, whereas higher values are an indication of higher fragility. While in principle there is no upper limit for m_A, on a practical ground the most fragile system seems to be tri-phenyl-phosphate, with $m_A \approx 160$.

A very similar definition has been proposed by Speedy:[25]

$$m_S \doteq \left. \frac{d\left[\dfrac{\log(\eta(T)/\eta_\infty)}{\log(\eta(T_g)/\eta_\infty)}\right]}{d(T_g/T)} \right|_{T=T_g}. \tag{2}$$

At a first sight, it seems that a trivial normalization factor would bring us from m_S to m_A. However, this expression becomes 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

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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 η_∞, although small, has been washed out. It is worth pointing out, however, that for all 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_S ranges from one for strong glasses to ≈ 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 an intermediate temperature (also see 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 η_∞ and 10^{13} Poise), $F_{1/2}$ is defined as $F_{1/2}=2(T_g/T^*)-1$. It is worth mentioning 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 glassformers.[30]

Finally, a generalized, temperature-dependent fragility (either m_A or m_S) is sometimes 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 as $m_A(T)$ and $m_S(T)$, with the implicit definition that when the argument is missing, the quantities are calculated at $T=T_g$.

B. 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]

$$\eta(T)=\eta_\infty \exp\left(\frac{DT_0}{T-T_0}\right), \tag{3}$$

where η_∞, D and T_0 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:[5]

$$T_g=T_0\left(1+\frac{D}{17\ln(10)}\right). \tag{4}$$

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

$$D=\frac{17\ln(10)}{m_S-1} \tag{5}$$

and, therefore, can be assumed to be a further fragility index. This index, which ranges from ∞ for strong liquids (actually $D\approx 100$ for vitreous silica) to ≈ 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]

$$F_{1/2}=\frac{m_S-1}{m_S+1}. \tag{6}$$

C. 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] Similar to the kinetic fragility that naturally emerges from the Angell plot [$\log(\eta)$ versus T_g/T for different systems], the vigor of the concept of thermodynamic fragility arises from the temperature dependence of the excess entropy $S_{ex}(T)$, defined as the difference between the entropy of the liquid and the entropy of the stable crystal. On plotting $S_{ex}(T_g)/S_{ex}(T)$ versus 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_A.

In analogy with m_A (or with m_S), 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

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$$m_T \doteq \left.\frac{d(S_{\rm ex}(T_g)/S_{\rm ex}(T))}{d(T_g/T)}\right|_{T=T_g} = T_g \frac{S'_{\rm ex}(T_g)}{S_{\rm ex}(T_g)}, \tag{7}$$

$S'_{\rm ex}(T)$ being the temperature derivative of $S_{\rm ex}(T)$.

D. Relation between kinetic and thermodynamic fragility

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

$$\tau(T) = \tau_\infty \exp\left(\frac{\mathcal{E}}{T\Sigma(T)}\right), \tag{8}$$

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

$$\eta(T) = \eta_\infty \exp\left(\frac{\mathcal{E}}{T\Sigma(T)}\right), \tag{9}$$

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 $T_{\rm K}$), where the configurational entropy vanishes. If both the Adam–Gibbs [Eq. (9)] and Vogel–Tamman–Fulcher relations [Eq. (3)] are valid, then necessarily T_0 and $T_{\rm K}$ are equal one to each other. This equality has been recently disputed.[35] We do not discuss this problem further, with the aim of studying 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 $T_0 = T_{\rm K}$). 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,[36] even if other studies indicate the failure of such a proportionality.[37] Assuming that the Adam–Gibbs relation correctly describes the T dependence of the viscosity in a supercooled liquids, by plugging Eq. (9) into the definition of m_S, Eq. (2), we get [using $\eta(T_g)/\eta_\infty = 10^{17}$]:

$$m_S = 1 + T_g \frac{\Sigma'(T_g)}{\Sigma(T_g)}, \tag{10}$$

and, recalling Eq. (7), we have the desired relation between kinetic and thermodynamic fragility:

$$m_S = 1 + m_T. \tag{11}$$

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

III. 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 Σ, 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.

A. Gaussian model

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

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

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

$$\Sigma(e) = k_{\rm B}N\left[\alpha - \frac{(e-e_o)^2}{\bar{\epsilon}^2}\right], \tag{13}$$

being $\bar{\epsilon} = \epsilon/\sqrt{N}$. In this expressions α counts the total number of states [it is the maximum of $\Sigma(e)/N$ in $k_{\rm B}$ 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[44,45]

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

we get

$$e(T) = e_o - \frac{\bar{\epsilon}^2}{2k_{\rm B}T}, \tag{15}$$

and, finally, inserting Eq. (15) into Eq. (13), we have the explicit expression of the configurational entropy as a function of the temperature:

$$\Sigma(T) = k_{\rm B}N\left[\alpha - \frac{\bar{\epsilon}^2}{(2k_{\rm B}T)^2}\right]. \tag{16}$$

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From Eq. (13), the Kauzmann energy e_K, i.e., the energy where $\Sigma(e)=0$, is promptly derived:

$$e_K = e_o - \bar{\epsilon}\sqrt{\alpha}, \tag{17}$$

and, plugging the Kauzmann energy [Eq. (17)] in Eq. (15), we find the Kauzmann temperature:

$$k_B T_K = \frac{\bar{\epsilon}}{2\sqrt{\alpha}}. \tag{18}$$

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), to obtain

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

Once we have a model for the configurational entropy, we can—applying Eq. (10)—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

$$m_S = \frac{T_g^2 + T_K^2}{T_g^2 - T_K^2}. \tag{20}$$

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. Another possible selection of parameters, and thus other expressions for the fragility, are of course possible. Equation (20) (as well as similar expressions for other landscape models; see below) makes clear the well-known fact that the fragility is somehow related to the "distance" between T_g and T_K: the higher the ratio T_g/T_K the strongest the liquid.

As a final 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

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

with $D = \mathcal{E}/(\alpha N k_B T_K)$, 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 ($T \gg T_k$), $D' \to D$ while in the low-T regime (T approaching T_k) $D' \to D/2$.

B. Hyperbolic model

For 30 years it has been realized[46] that the temperature dependence of the (constant volume) excess specific heat can be described by a hyperbolic law ($C \approx \text{const} + \text{const}'/T$), and this law is commonly used to represent the experimental data.[27] 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.[47] In Ref. 47, 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 Ref. 48, 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 behavior 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 Eqs. (3) and (9), it turns out an explicit temperature dependence for $\Sigma(T)$:

$$\Sigma(T) = \frac{\mathcal{E}}{D T_K}\left[1 - \frac{T_K}{T}\right]. \tag{22}$$

It is implicit in this expression the coincidence of T_0 and T_K. This equation can be cast in form very similar to Eq. (16) by defining the quantities α and $\bar{\epsilon}$:

$$\alpha \doteq \frac{\mathcal{E}}{D N k_B T_K}, \tag{23}$$

$$\bar{\epsilon} \doteq \frac{2\mathcal{E}}{DN} = 2 k_B T_K \alpha. \tag{24}$$

As we will see soon, α 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 α. Rewriting Eq. (22) with the elimination of $\mathcal{E}$ and D in favor of α and $\bar{\epsilon}$, we have

$$\Sigma(T) = k_B N \left[\alpha - \frac{\bar{\epsilon}}{2 k_B T}\right], \tag{25}$$

an expression that can be directly compared with Eq. (16), or, expressing the prefactor in Eq. (22) in terms of α via Eq. (23),

$$\Sigma(T) = k_B N \alpha \left[1 - \frac{T_K}{T}\right], \tag{26}$$

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):

$$e(T) = e_R + \int_{T_R}^{T} T \frac{d\Sigma}{dT} dT = e_R + \alpha k_B T_K \ln(T/T_R), \tag{27}$$

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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. (25) we get

$$\Sigma(e)=Nk_{\mathrm{B}}\alpha\left[1-\frac{T_{\mathrm{K}}}{T_R}\exp\left(-\frac{2(e-e_R)}{\bar{\epsilon}}\right)\right]. \tag{28}$$

Obviously, we can eliminate T_R from this equation, by properly redefining e_R. A useful possibility is to choose $T_R=T_{\mathrm{K}}$; then, from Eq. (27), $e_R=e_{\mathrm{K}}$ and

$$\Sigma(e)=Nk_{\mathrm{B}}\alpha\left[1-\exp\left(-\frac{2(e-e_{\mathrm{K}})}{\bar{\epsilon}}\right)\right]. \tag{29}$$

At variance with the configurational entropy of the Gaussian model, the present $\Sigma(e)$ does not show any maxima; rather it increases continuously, asymptotically approaching the value $Nk_{\mathrm{B}}\alpha$.

From Eq. (26), using Eq. (10), we can easily determine the fragility of this model:

$$m_S=\frac{T_g}{T_g-T_{\mathrm{K}}}. \tag{30}$$

It is worth pointing out that this expression is the expansion of the fragility of the Gaussian model to first order in T_g-T_{K}.

C. Logarithmic (or binomial) model

The previous two models for the configurational entropy share the property that $d\Sigma/de$ is nondiverging at $e=e_{\mathrm{K}}$, so the Kauzmann temperature exists and it is nonvanishing. In order to introduce a more flexible model, embedding the possibility of having a vanishing Kauzmann temperature, Debenedetti, Stillinger, and Shell[49] recently proposed a modification of the Gaussian model that, with a slight change in notation with respect to the original definition, reads as

$$\Sigma(e)=Nk_{\mathrm{B}}\alpha\left\{(1-\gamma)\left[1-\left(\frac{u}{\sqrt{\alpha}}\right)^2\right]+\gamma\left[1-\frac{\left(1+\frac{u}{\sqrt{\alpha}}\right)\ln\left(1+\frac{u}{\sqrt{\alpha}}\right)+\left(1-\frac{u}{\sqrt{\alpha}}\right)\ln\left(1-\frac{u}{\sqrt{\alpha}}\right)}{2\ln(2)}\right]\right\}, \tag{31}$$

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

$$u=\frac{e-e_o}{\bar{\epsilon}}. \tag{32}$$

This is a linear combination-weighted by the parameter γ-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., a model for the thermodynamics of a gas of binary excitations.[50] It has been used to model the thermodynamics of supercooled liquids and the T dependence of the inherent structure energy.[50] Obviously, the logarithmic term in Eq. (31) become dominant in the low-T/low-$(e-e_{\mathrm{K}})$ 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

$$\Sigma(e)=Nk_{\mathrm{B}}\alpha\left[1-\frac{\left(1+\frac{u}{\sqrt{\alpha}}\right)\ln\left(1+\frac{u}{\sqrt{\alpha}}\right)+\left(1-\frac{u}{\sqrt{\alpha}}\right)\ln\left(1-\frac{u}{\sqrt{\alpha}}\right)}{2\ln(2)}\right]. \tag{33}$$

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, $e_{\mathrm{K}}=e_o-\bar{\epsilon}\sqrt{\alpha}$. At this energy, the derivative of $\Sigma(e)$ shows a logarithmic divergence, thus implying that the Kauzmann temperature must vanish. Similar to the Gaussian model, the parameter e_o is the energy of the "top of the landscape" and α represents the maximum of $\Sigma(e)/Nk_{\mathrm{B}}$. 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 $v=(e-e_{\mathrm{K}})/\bar{\epsilon}$ as

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$$\Sigma(e)=Nk_{\mathrm{B}}\alpha\left[1-\frac{\frac{v}{\sqrt{\alpha}}\ln\left(\frac{v}{\sqrt{\alpha}}\right)+\left(2-\frac{v}{\sqrt{\alpha}}\right)\ln\left(2-\frac{v}{\sqrt{\alpha}}\right)}{2\ln(2)}\right]. \tag{34}$$

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:

$$e(T)-e_o=-\bar{\epsilon}\sqrt{\alpha}\tanh\left[\frac{2\ln(2)\bar{\epsilon}}{\sqrt{\alpha}k_{\mathrm{B}}T}\right], \tag{35}$$

and inserting this expression in Eq. (34), the temperature dependence of the configurational entropy is promptly derived:

$$\Sigma(T)=Nk_{\mathrm{B}}\alpha\left\{\frac{1}{\ln(2)}\ln\left[2\cosh\left(\frac{\ln(2)\bar{\epsilon}}{\sqrt{\alpha}k_{\mathrm{B}}T}\right)\right]-\frac{\bar{\epsilon}}{\sqrt{\alpha}k_{\mathrm{B}}T}\tanh\left(\frac{\ln(2)\bar{\epsilon}}{\sqrt{\alpha}k_{\mathrm{B}}T}\right)\right\}. \tag{36}$$

As a consequence of the infinite value of $d\Sigma(e)/de$ at e_{K}, this function does vanish only at $T=0$, i.e., for this model $T_{\mathrm{K}}=0$. It is convenient, for the 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

$$T_{\mathrm{K}}^{*}=\frac{1}{3}\ln(2)\frac{\bar{\epsilon}}{k_{\mathrm{B}}\sqrt{\alpha}}, \tag{37}$$

whose value is very close to the "apparent" Kauzmann temperature that would have been identified by extrapolating Eq. (36) toward zero using only information on $\Sigma(T)$ at "high" temperature, similar 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 $k_{\mathrm{B}}T_{\mathrm{K}}\sqrt{\alpha}/\bar{\epsilon}\approx 0.23\,[\approx\ln(2)/3]$. Having introduced the "apparent" Kauzmann temperature for the logarithmic model, we can write Eqs. (35) and (36) as

$$e(T)-e_o=\frac{3}{\ln(2)}\alpha k_{\mathrm{B}}T_{\mathrm{K}}^{*}\tanh\left(\frac{3T_{\mathrm{K}}^{*}}{T}\right),$$
$$\Sigma(T)=\frac{Nk_{\mathrm{B}}\alpha}{\ln(2)}\left\{\ln\left[2\cosh\left(\frac{3T_{\mathrm{K}}^{*}}{T}\right)\right]-\frac{3T_{\mathrm{K}}^{*}}{T}\tanh\left(\frac{3T_{\mathrm{K}}^{*}}{T}\right)\right\}. \tag{38}$$

Once the explicit T dependence of $\Sigma(T)$ is known, both the fragility m_S, defined in Eq. (10), and the T dependence of the viscosity (from the Adam–Gibbs equation) can be worked out. The two expressions read as

$$m_S=1+\left(\frac{3T_{\mathrm{K}}^{*}}{T_g}\right)^2\left\{\cosh^2\left(\frac{3T_{\mathrm{K}}^{*}}{T_g}\right)\ln\left[2\cosh\left(\frac{3T_{K}^{*}}{T_g}\right)\right]-\left(\frac{3T_{\mathrm{K}}^{*}}{T_g}\right)\cosh\left(\frac{3T_{\mathrm{K}}^{*}}{T_g}\right)\sinh\left(\frac{3T_{\mathrm{K}}^{*}}{T_g}\right)\right\}^{-1}, \tag{39}$$

$$\eta(T)=\eta_{\infty}\exp\left\{\frac{\ln(2)}{3}D\left(\frac{3T_{\mathrm{K}}^{*}}{T_g}\right)\left\{\ln\left[2\cosh\left(\frac{3T_{\mathrm{K}}^{*}}{T}\right)\right]-\left(\frac{3T_{\mathrm{K}}^{*}}{T_g}\right)\tanh\left(\frac{3T_{\mathrm{K}}^{*}}{T}\right)\right\}^{-1}\right\}. \tag{40}$$

D. Summary of models

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

(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 $v=(e-e_{\mathrm{K}})/\bar{\epsilon}$ 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 terms of e_o, α, 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 terms 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 $D=\mathcal{E}/(\alpha Nk_{\mathrm{B}}T_{\mathrm{K}})$.

In Fig. 1 we sketched the e-dependence of the configurational energy for the examined models: Gaussian (full line), hyperbolic (dashed line), and logarithmic (dot–dashed line). As an example, the three configurational entropies are reported for the specific case of $\alpha=0.8$ [as the scaling of $\Sigma(e)$ with α for the hyperbolic model is different from that for the Gaussian and logarithmic models, we cannot use a reduced variable].

Similarly, in Figs. 2 and 3 we report the corresponding configurational entropy as a function of T/T_{K} and T_{K}/T, respectively. In the case of the logarithmic model T_{K}^{*} defined in Eq. (37) is used to scale the temperatures.

In Fig. 4 we report the temperature dependence of the energy elevation (normalized to the factor $\alpha k_{\mathrm{B}}T_{\mathrm{K}}$) 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 nonphysical continued rise of $e(T)$ on increasing T.

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

E. Gaussian models with nonconstant vibrational entropy

All the discussions in the previous sections were based on the assumption that the *vibrational* entropy associated to a given basin is independent from the energy elevation of the

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TABLE I. A summary of the main relations relating the relevant quantities (left column) for the three configurational entropy models introduced before. The relation that defines the model is reported in the 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 $3T_K^*/T_g$. In the case of the logarithmic model, T_K^* is used [see Eq. (37)] in place of the Kauzmann temperature.

	Gaussian model	Hyperbolic model	Logarithmic model
$\Sigma(e)/Nk_B$ {	$\boxed{\alpha-u^2}$	$a[1-\exp(-2u)]$	$\boxed{\alpha\left[1-\frac{1}{2\ln(2)}\left[\left(1+\frac{u}{\sqrt{\alpha}}\right)\ln\left(1+\frac{u}{\sqrt{\alpha}}\right)+\left(1-\frac{u}{\sqrt{\alpha}}\right)\ln\left(1-\frac{u}{\sqrt{\alpha}}\right)\right]\right]}$
	$-v^2+2\sqrt{\alpha}v$	$\alpha[1-\exp(-2v)]$	$\alpha\left[1-\frac{1}{2\ln(2)}\left[\frac{v}{\sqrt{\alpha}}\ln\left(\frac{v}{\sqrt{\alpha}}\right)+\left(2-\frac{v}{\sqrt{\alpha}}\right)\ln\left(2-\frac{v}{\sqrt{\alpha}}\right)\right]\right]$
e_K	$e_o-\bar{\epsilon}\sqrt{\alpha}$	e_o	$e_o-\bar{\epsilon}\sqrt{\alpha}$
k_BT_K	$\frac{\bar{\epsilon}}{2\sqrt{\alpha}}$	$\frac{\bar{\epsilon}}{2\alpha}$	$\frac{\ln(2)}{3}\frac{\bar{\epsilon}}{\sqrt{\alpha}}$
$\bar{\epsilon}$	$2\sqrt{\alpha}k_BT_K$	$2\alpha k_BT_K$	$\frac{3}{\ln(2)}\sqrt{\alpha}k_BT_K^*$
$e(T)-e_o$	$-2\alpha k_BT_K\left(\frac{T_K}{T}\right)$	$\alpha k_BT_K\ln\left(\frac{T}{T_K}\right)$	$-\frac{3}{\ln(2)}\alpha k_BT_K^*\tanh\left(\frac{3T_K^*}{T}\right)$
$e(T)-e_K$	$2\alpha k_BT_K\left(1-\frac{T_K}{T}\right)$	$\alpha k_BT_K\ln\left(\frac{T}{T_K}\right)$	$\frac{3}{\ln(2)}\alpha k_BT_K^*\left[1-\tanh\left(\frac{3T_K}{T}\right)\right]$
$\Sigma(T)/Nk_B$	$\alpha\left[1-\left(\frac{T_K}{T}\right)^2\right]$	$\alpha\left[1-\left(\frac{T_K}{T}\right)\right]$	$\frac{\alpha}{\ln(2)}\left\{\ln\left[2\cosh\left(\frac{3T_K^*}{T}\right)\right]-\frac{3T_K}{T}\tanh\left(\frac{3T_K^*}{T}\right)\right\}$
m_S	$\frac{T_g^2+T_K^2}{T_g^2-T_K^2}$	$\frac{T_g}{T_g-T_K}$	$1+w^2\{\cosh^2(w)\ln[2\cosh(w)]-w\cosh(w)\sinh(w)\}^{-1}$
$\ln(\eta(T)/\eta_\infty)$	$\frac{DT_K}{T-T_K}\frac{T}{T+T_K}$	$\boxed{\frac{DT_K}{T-T_K}}$	$\left\{\frac{\ln(2)}{3}D\frac{3T_K^*}{T}\left\{\ln\left[2\cosh\left(\frac{3T_K^*}{T}\right)\right]-\frac{3T_K^*}{T}\tanh\left(\frac{3T_K^*}{T}\right)\right\}^{-1}\right\}$

minimum of the basin itself. These assumptions 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 a series of $e-e_K$ and retain only the first-order term, an approximation certainly valid for low enough temperatures:

$$S_v(e)=S_v^K+\left.\frac{dS_v}{de}\right|_{e=e_K}(e-e_K). \tag{41}$$

The quantity dS_v/de is a further system-dependent parameter. For sake of simplicity let us define as parameter a "vibrational" temperature T_v via

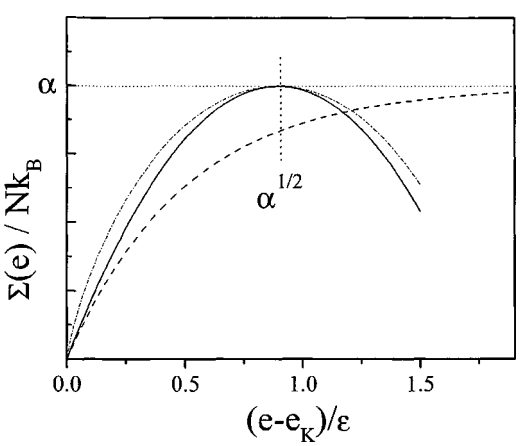

FIG. 1. A sketch of the energy dependence of the configurational energy for three models: Gaussian (full line), hyperbolic (dashed line), and logarithmic (dot–dashed line). The reduced entropy $\Sigma(e)/Nk_B$ is plotted as a function of $(e-e_K)/\bar{\epsilon}$ for the specific case of $\alpha=0.8$.

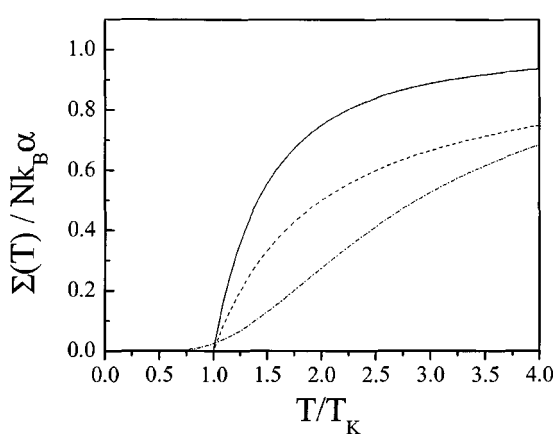

FIG. 2. A plot of the temperature dependence of the configurational entropy for three models: Gaussian (full line), hyperbolic (dashed line), and logarithmic (dot–dashed line). The reduced entropy $\Sigma(T)/Nk_B$ further normalized to α is plotted as a function of T/T_K. In the case of the logarithmic model, T_K^* defined in Eq. (37) is used in substitution of T_K.

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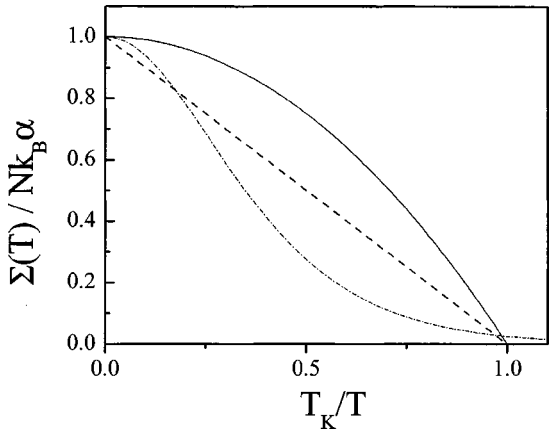

FIG. 3. Similar to Fig. 2, the temperature dependence of the configurational entropy for three models [Gaussian (full line), hyperbolic (dashed line), and logarithmic (dot–dashed line)] is plotted as a function of T_K/T. In the case of the logarithmic model T_K defined in Eq. (37) is used in the substitution of T_K.

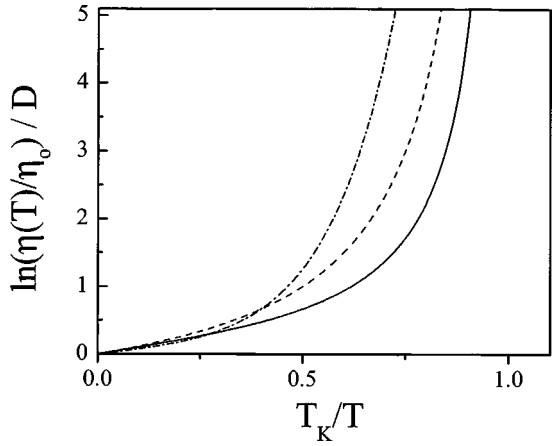

FIG. 5. A plot of the temperature dependence of the viscosity for three models: Gaussian (full line), hyperbolic (dashed line), and logarithmic (dot–dashed line). The logarithm of the viscosity normalized by $\eta(T_\infty)$, normalized to D, is plotted as a function of T_K/T. In the case of the logarithmic model T_K^* defined in Eq. (37) is used in substitution of T_K.

$$\frac{N}{T_v}=\left.\frac{dS_v}{de}\right|_{e=e_K}. \tag{42}$$

The calculation proceeds along the same line outlined in the case of the Gaussian model. First, from the generalization of Eq. (14), i.e., from

$$\frac{1}{T}=\frac{dS/N}{de}=\frac{d\Sigma(e)/N}{de}+\frac{dS_v/N}{de}=\frac{d\Sigma(e)/N}{de}+\frac{1}{T_v}, \tag{43}$$

we get the temperature dependence of the energy of the visited minima:

$$e(T)=e_o-\frac{\overline{\epsilon}^2}{2}\left(\frac{1}{k_BT}-\frac{1}{k_BT_v}\right), \tag{44}$$

and inserting Eq. (44) into the definition of the Gaussian model, Eq. (13), we have the explicit expression of the configurational entropy as a function of the temperature:

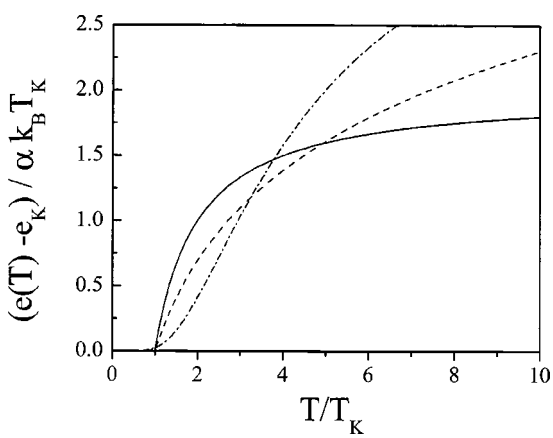

FIG. 4. A plot of the temperature dependence of the energy elevation for three models: Gaussian (full line), hyperbolic (dashed line), and logarithmic (dot–dashed line). The energy elevation $e-e_K$, normalized to k_BT_K, and further normalized to α, is plotted as a function of T/T_K. In the case of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

$$\Sigma(T)=k_BN\left[\alpha-\frac{\overline{\epsilon}^2}{4}\left(\frac{1}{k_BT}-\frac{1}{k_BT_v}\right)^2\right]. \tag{45}$$

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

$$\overline{\epsilon}=2\sqrt{\alpha}k_BT_K\left(\frac{T_v}{T_v-T_K}\right); \tag{46}$$

thus, substituting this expression in Eq. (45),

$$\Sigma(T)=k_BN\alpha\left[1-\left(\frac{T_K}{T_v-T_K}\right)^2\left(\frac{T_v}{T}-1\right)^2\right]. \tag{47}$$

Through the configurational entropy, we can apply Eq. (10) to find an expression for the fragility:

$$m_S=\frac{(T_g^2+T_K^2)-2T_gT_K(T_g/T_v)}{(T_g^2-T_K^2)-2T_K(T_g-T_K)(T_g/T_v)}. \tag{48}$$

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

$$\eta(T)=\eta_\infty\exp\left[\frac{DT_K}{T-T_K}\frac{T}{T+T_K-2T(T_K/T_v)}\left(\frac{T_v-T_K}{T_v}\right)^2\right], \tag{49}$$

with, as before, $D=\mathcal{E}/(\alpha Nk_BT_K)$.

Similar to Fig. 3, in Fig. 6 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.

Analogously, Fig. 7 shows the temperature dependence of the viscosity, as predicted by the Gaussian model, with energy-dependent vibrational entropy for different values of T_v/T_K. As it can be noticed, it seems that the values of T_v

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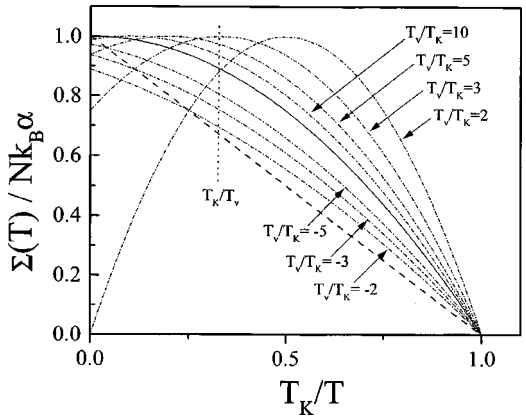

FIG. 6. Similar to Fig. 2, the temperature dependence of the configurational entropy is reported for the Gaussian model with energy-dependent vibrational entropy for different values of the parameter T_v/T_K (dot–dashed line). For comparison, also the two corresponding function for the Gaussian (full line) and hyperbolic (dashed line) models are reported.

allows one to interpolate between the behavior of the Gaussian model (obviously reached for $T_v \to \infty$ or $-\infty$) and that of the hyperbolic model (that is approximately obtained for $T_v/T_K \approx -1 \backslash -1.5$). It is worth remembering that, in most numerical simulations of model liquids, T_v is found to be negative for constant density (thus constant PEL) simulations, while $T_v > 0$ for constant pressure simulations.[51] In the case of a model for water, the sign of T_v has been found to be density dependent.[43,52] On the experimental side, at constant pressure, the sign of T_v turns out to be both positive[37] and negative,[53] depending on the specific system.

Finally, in Table II we report the relevant expression relative to the Gaussian model with energy-dependent vibrational entropy ($T_v \neq \infty$) compared with those of the Gaussian model ($T_v = \infty$).

IV. 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." Second, 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.

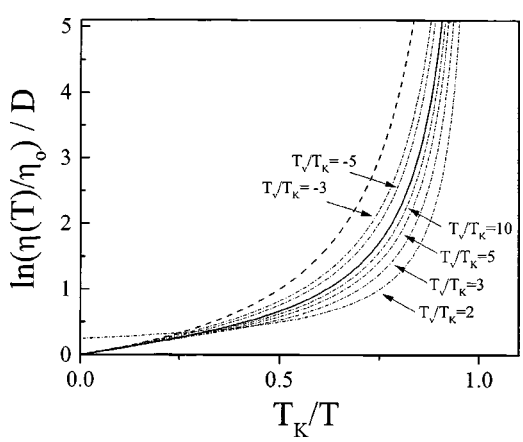

FIG. 7. Similar to Fig. 5, the temperature dependence of the viscosity is reported for the Gaussian model with energy-dependent vibrational entropy for different values of the parameter T_v/T_K (dot–dashed line). For comparison, also the two corresponding function for the Gaussian (full line) and hyperbolic (dashed line) models are reported.

TABLE II. A summary of the main relations relating the relevant quantities (left column) for the Gaussian configurational entropy models: the simple Gaussian model ($T_v = \infty$) and the Gaussian model with energy-dependent vibrational entropy.

	$\frac{\delta S_v}{de}=0$	$\frac{dS_v}{de}\neq 0$
$k_B T_K$	$\frac{\bar{\epsilon}}{2\sqrt{\alpha}}$	$\frac{k_B T_v \bar{\epsilon}}{2\sqrt{\alpha} k_B T_v + \bar{\epsilon}}$
$\bar{\epsilon}$	$2\sqrt{\alpha} k_B T_K$	$2\sqrt{\alpha} k_B T_K \left[\frac{T_v}{T_v - T_K}\right]$
$e(T)-e_o$	$2\alpha k_B T_K \left(\frac{T_K}{T}\right)$	$2\alpha k_B T_K \left[\frac{T_v T_K}{(T_v - T_K)^2}\right]\left[\frac{T_v}{T}-1\right]$
$\Sigma(T)/Nk_B$	$\alpha\left[1-\left(\frac{T_K}{T}\right)^2\right]$	$\alpha\left[1-\left(\frac{T_K}{T_v - T_K}\right)^2\left(\frac{T_v}{T}-1\right)^2\right]$
m_S	$\frac{T_g^2+T_K^2}{T_g^2-T_K^2}$	$\frac{(T_g^2+T_K^2)-2T_g T_K(T_g/T_v)}{(T_g^2+T_K^2)-2T_K(T_g-T_K)(T_g/T_v)}$
$\ln(\eta(T)/\eta_\infty)$	$\frac{DT_K}{T-T_K}\frac{T}{T+T_K}$	$\frac{DT_K}{T-T_K}\frac{T}{T+T_K-2T(T_K/T_v)}\left[\frac{T_v-T_K}{T_v}\right]^2$

A. Speedy's expression of fragility

In 1999, Speedy[25]—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 terms of α and $\Sigma(T_g)$ ["$\Delta_g^l S(T_g)$" 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 α holds only if one neglects the possibility that $\Sigma(T_g)$, a system-dependent quantity, depends on α. In principle, its implicit dependence on α can also reverse the fragility–number of states relation.

B. Sastry's expression of fragility

More recently, another expression for the fragility in terms 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 as to relate [compare Eqs. (9) and (3)] the configurational entropy to the coefficient D, which, as discussed before, is an index of kinetic fragility (actually, Sastry

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reports his expression for the fragility $K=1/D$), and (ii) the coincidence of T_0 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 (39), however, we can put the quantity δS (in Sastry's notation) equal to zero. The Sastry expression becomes (with the change of notation from σ to $\bar{\epsilon}$)

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

Here "T_g" is the MD glass transition temperatures. In Eq. (51) we have explicitly included the Adam–Gibbs constant $\mathcal{E}$ that was implicitly assumed constant and landscape-independent in Ref. 26 (see also Ref. 54).

After the conversion from K to m_S, using Eq. (5), we have

$$m_S=17\ln(10)\frac{\bar{\epsilon}\sqrt{\alpha}}{2\mathcal{E}}\left(1+\frac{T_K}{T_g}\right)+1. \tag{52}$$

Similar to Eq. (50), also this equation cannot be used to predict the α dependence of the fragility. Indeed, α appears here explicitly but also implicitly, via the system-dependent quantities T_g 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 hypotheses (i)–(iii) can only be consistent if one uses a low-temperature expansion of $\Sigma(T)$.

C. 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 us suppose to have a hypothetical system, fully defined by a Gaussian landscape with a given value of the relevant parameters α, ϵ, and e_o. The temperature dependence of the viscosity in this model is reported in Eq. (21). To set up an Angell plot, we need to define the "glass transition temperature" T_g. As done experimentally, once the T dependence of the viscosity is known, T_g is defined from the condition $\log(\eta(T_g)/\eta_\infty)=17$. Using Eq. (21), the solution of this equation for (positive) T_g is

$$T_g=T_K\left\{\frac{1}{2}\frac{D}{17\ln(10)}+\sqrt{1+\frac{1}{4}\left(\frac{D}{17\ln(10)}\right)^2}\right\}, \tag{53}$$

with $D=\mathcal{E}/(\alpha N k_B T_K)=2\mathcal{E}/(\sqrt{\alpha}N\bar{\epsilon})$. For the sake of compactness, let us define the function $\gamma(x)$:

$$\gamma(x)=\frac{1}{2}\frac{x}{17\ln(10)}+\sqrt{1+\frac{1}{4}\left(\frac{x}{17\ln(10)}\right)^2}, \tag{54}$$

so that

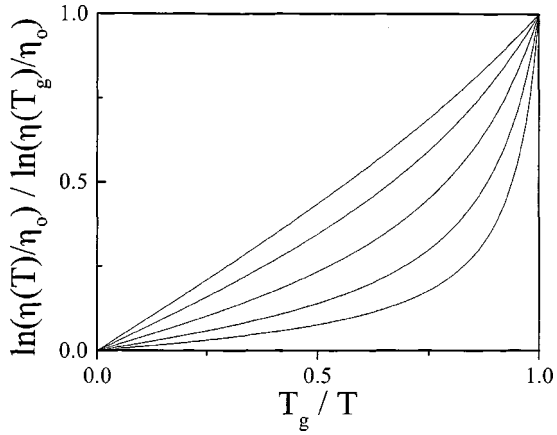

FIG. 8. Reconstructed Angell plot ($[\log(\eta(T)/\eta_\infty)]/[\log(\eta(T_g)/\eta_\infty)]$ vs T_g/T) for the case of the Gaussian model. The different curves correspond to different $\mathcal{E}$ values: from top to bottom $\mathcal{E}=80$, 40, 20, 10 and 5 in units of $\sqrt{\alpha}N\bar{\epsilon}/2$.

$$T_g=T_K\gamma(D). \tag{55}$$

Obviously, the expression of T_g, besides the trivial temperature scale T_K, depends on the parameter $D(=2\mathcal{E}/(\sqrt{\alpha}N\bar{\epsilon}))$ that, in turn, embodies the information on the "number of states" but also from quantities distinct from the statistics of the minima (specifically from the parameter $\mathcal{E}$). We want now to plot the rescaled logarithmic viscosity $y(T)\equiv[\log(\eta(T)/\eta_\infty)]/[\log(\eta(T_g)/\eta_\infty)]$ 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 $\eta(T)$ reported in Eq. (21), to

$$y(T)=\frac{D}{17\ln(10)}\frac{T_K}{T-T_K}\frac{T}{T+T_K}. \tag{56}$$

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

$$y(T)=\left(\frac{T_g}{T}\right)\frac{\gamma(D)^2-1}{\gamma(D)^2-\left(\frac{T_g}{T}\right)^2}. \tag{57}$$

In Fig. 8 we have reported the quantity $y(T)$ of Eq. (57) versus T_g/T, i.e., we have made an Angell plot, for different values of the parameter $\mathcal{E}$ at fixed α 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 $\mathcal{E}$ 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 α and $\bar{\epsilon}$), we can have a strong system (large $\mathcal{E}$) as well as a fragile one (small $\mathcal{E}$). 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.*[56] This statement, and the role of the effective barrier height in determining the fragility of a glass, has been already discussed in the literature (see,

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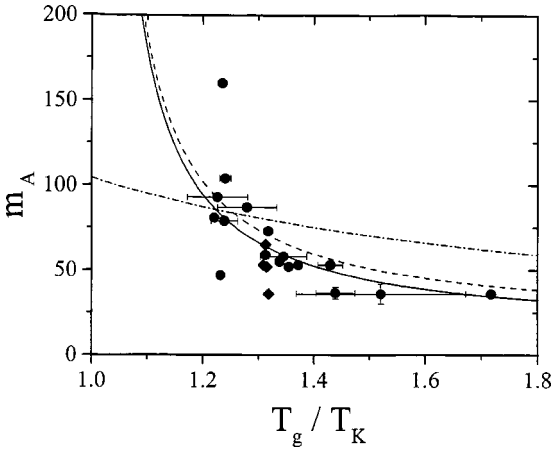

FIG. 9. Experimental values of the kinetic fragility m_A plotted as a function of the ratio T_g/T_K for those systems where the three quantities (m_A, T_g, and T_K) are available. The input data are reported in Table III. For those systems where more than one determination of the parameters is known, we have reported in the plot the average value together with an "error" bar that indicates the whole dispersion.

TABLE III. A summary of the quantity relevant to test Eq. (20) (T_g, T_K, and m_S) for those systems where the three quantities 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.

	T_g	T_K	m_A	Ref.
2-metylpentane	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
Triphenil phospate	205	166	160	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_2S_3	455	265	36	24, 55
$CaAl_2Si_2O_8$	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

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 $\mathcal{E}$ 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 $\mathcal{E}$ and the PEL properties and on the physical range of values of $\mathcal{E}$.

D. 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 $\mathcal{E}$ 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 e 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 $\mathcal{E}$, a strong system (large $\mathcal{E}$) would visit the "top-of-the-landscape," while a fragile system (small $\mathcal{E}$) 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_A are known (see Table III), the fragility m_A as a function of T_g/T_K (symbols). Also shown in the same figure are the predictions of Eqs. (20), (30), (39) (lines). A few points must be underlined: (i) there is rather good general agreement, but the single systems does not strictly verify any 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_v. 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 Eqs. (20) and (30) are so small that the experimental data do not allow us to discriminate among these two different landscape models, while the (pure) logarithmic model seems to be definitively unacceptable. Most likely, a Gaussian model with a small logarithmic correction would still be 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 us to firmly establish the general validity of one of the three models, 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 behavior is the actual one. Different systems have different value of α and may even not be described by a common landscape model. A typical example, one that it is worth discussing here, is the case of silica. As shown by Horbach and Kob,[58] vitreous silica (as described by the BKS potential model[59]) shows a strong T dependence of the fragility. More specifically, v-SiO_2, which is a well-known strong system close to the glass transition temperature, turns toward a more fragile behavior 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 fluoride.[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

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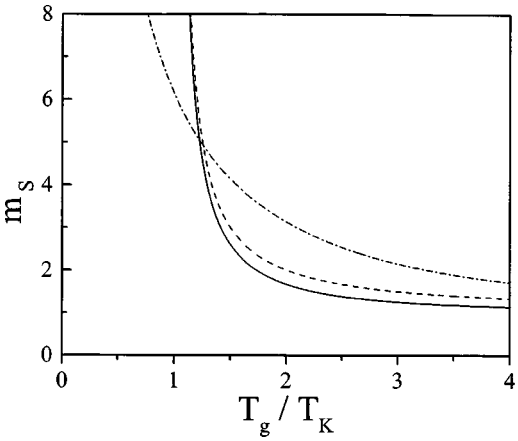

FIG. 10. Temperature dependence of the fragility for the three examined models: Gaussian (full line), hyperbolic (dashed line) and logarithmic (dot–dashed line). The quantity m_S is reported as a function of T_g/T_K.

BKS interaction potential model—is far from being "Gaussian." More specifically, they found that $\Sigma(T)$—at low T—shows a tendency toward 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, and this could be in agreement with the simulation results of Ref. 63 as the low statistics in the tail of $\Omega_N(E)$—as measured by MD—does not allow us to safely determine $d\Sigma(e)/de$ evaluated at e_K.

The logarithmic model, however, similar to the other models presented before, is not capable of catching the physics of the strong-to-fragile transition. Indeed, the fragility expressions for all the examined models [Eqs. (20), (30), (39)] show a *monotonic T* dependence, with a tendency toward a *decrease* of the fragility on increasing temperature (see Fig. 10). A behavior opposite to that is 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. What is actually sufficient (necessary?) for a strong to fragile transition—i.e., to have a maximum in the m_S versus T_g/T_K function—is that the configurational entropy—as a function of T—had a nonzero limit for $T\rightarrow 0$. 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 nonzero $\Sigma(T)$. 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, $\Sigma'(T)\rightarrow 0$, 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 a short-range interaction (non-mean field systems) poses several problems (see the discussion in Ref. 49), and is certainly calling for a further investigation.

V. DISCUSSION AND CONCLUSION

In conclusion, in this paper we have first summarized the main definitions of fragility; then we have recalled and studied different models for the configurational entropy 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 $\mathcal{E}$ entering in the numerator of the exponent of the Adam–Gibbs equation. On a general ground, the fragility of a system depends on the ratio $\mathcal{E}/\alpha N k_B T_K$.

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 $\mathcal{E}$ and would explore the "top-of-the-landscape," while the most fragile ones would have small $\mathcal{E}$ 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 $\mathcal{E}$, and in this case strong glass would have a small number of states (small α), at variance to the fragile systems with more states (large α). 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 nonvanishing zero-point entropy. This is an interesting possibility that deserves deeper investigation.

Overall, the present discussion, which heavily builds 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-type) configurational entropy (let us call these systems class A strong glass-forming materials). On the other side we find the—let us 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 of 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[64] that $\Sigma_c(T)$ along isochoric and isobaric paths are very close to each other. Similarly, in a very recent work,[65] Tarjus and co-workers 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, a large deviation ($\approx$40%) between constant density

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and constant pressure fragilities has been observed.[46] This ongoing discussion, 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.

ACKNOWLEDGMENTS

We acknowledge very useful discussions with G. Parisi and S. Sastry. We also thank L. Angelani, J. Dyre, S. Mossa, K. Ngai, S. Sastry, and R. Speedy for a critical reading of the manuscript and for helpful suggestions. A special thanks to Austen Angell for his invaluable suggestions that helped us in the preparation of this manuscript. We acknowledge support from Miur FIRB and Cofin and INFM.

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(i) the definition of m_T [Eq. (7)]; (ii) the definition of m_S [Eq. (2)]; and (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 highlights the need for dynamical information in the evaluation of the fragility.
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