Gaussian excitations model for glass-former dynamics and thermodynamics

Dmitry V. Matyushov

Department of Chemistry and Biochemistry and Department of Physics and Astronomy,
Arizona State University, PO Box 871604, Tempe, AZ 85287-1604

C. A. Angell

Department of Chemistry and Biochemistry, Arizona State University, PO Box 871604, Tempe, AZ 85287-1604

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We describe a model for the thermodynamics and dynamics of glass-forming liquids in terms of excitations from an ideal glass state to a Gaussian manifold of configurationally excited states. The quantitative fit of this three parameter model to the experimental data on excess entropy and heat capacity shows that “fragile” behavior, indicated by a sharply rising excess heat capacity as the glass transition is approached from above, occurs in anticipation of a first-order transition usually hidden below the glass transition to a “strong” liquid state of low excess entropy. The distinction between fragile and strong behavior of glass-formers is traced back to an order of magnitude difference in the Gaussian width of their excitation energies. 

I. INTRODUCTION

Viscous liquids close to the glass transition are usually characterized by a broad distributions of (their) relaxation times (stretched exponential kinetics) and stronger than Arrhenius (super-Arrhenius) dependence of the relaxation times on temperature. The stretched exponential kinetics is often represented by Kohlrausch-Williams-Watts (KWW) relaxation function

$$\phi^{KWW}(t) = \exp\left(-\left(t/\tau\right)^{\beta}\right),$$

where $\beta \leq 1$ is a stretching exponent and $\phi^{KWW}(t)$ is a normalized function representing some relaxing property. The temperature dependence of the relaxation time $\tau$ in this equation has been given many forms, but is most commonly represented by the empirical Vogel-Fulcher-Tammann (VFT) law

$$\ln(\tau/\tau_0) = DT_0/(T - T_0),$$

were $\tau_0$ is a characteristic time for liquid quasi-lattice vibrations. According to this equation, the relaxation time diverges at the VFT temperature $T_0$ below the glass transition temperature $T_g$; $T_0$ is close to $T_g$ for fragile liquids with super-Arrhenius kinetics and tends to zero for strong liquids with nearly Arrhenius relaxation.

At sufficiently low temperature, below the range of temperatures described by the mode-coupling theory, a liquid can be characterized by a set of minima (inherent structures) of the potential energy landscape divided by Stillinger into “basins of attraction” The relaxation then occurs by a sequence of activated transitions between basins or collections of basins separated by low barriers (metabasins) While opinions of its origin differ, there is much evidence for a dynamic crossover temperature in fragile liquids, usually corresponding to the critical temperature of mode coupling theory, where relaxation times are about $10^{-7}$ s. Phenomenological theories, usually operating below this critical tempera-
ture, differ in their attribution of the driving force responsible for activated events.

The Adam-Gibbs theory\textsuperscript{21} suggests that entropy controls the activation process. According to this line of thought,\textsuperscript{12,13,14} the divergence of the relaxation time at $T_0$ is caused by a decrease of the number of available states related to the configurational entropy $S_c(T)$. The relaxation time is given by the Adam-Gibbs relation

$$\ln(\tau/\tau_0) = \frac{\Delta}{T S_c(T)}$$

which anticipates a growing length-scale $\xi$ attributed to cooperatively rearranging regions. $\xi$ diverges as $S_c(T)^{-1}$ on approach to the Kauzmann temperature $T_K$ at which the configurational entropy vanishes:11,15,16

$$S_c(T_K) = 0.$$ (4)

The free volume theory\textsuperscript{17,18} also considers entropy as the driving force for the glass transition in terms of the volume available for reorganizing the liquid. This “free” volume becomes increasingly scarce on cooling, eventually leading to a divergent relaxation time at the VFT temperature. The analysis of $T$, $P$ viscosity data, however, indicates that it is temperature and not density that is the primary factor behind the super-Arrhenius kinetics.\textsuperscript{19}

The coefficient $\Delta$ in Eq. 9 can be related to system properties within the concept of entropic droplet.\textsuperscript{20,21,22} Following arguments by Bouchaud and Biroli\textsuperscript{20} and by Lubchenko and Wolynes,\textsuperscript{21} the probability of creation of a droplet of size $\xi$ is a competition of the surface, $\propto \xi^2$, and entropic bulk, $\propto \xi^3$, effects:

$$P(\xi) \propto \exp \left(-\sigma(\xi)\xi^2 + S_c(\xi)^3\right).$$ (5)

The probability minimizes at the stationary point of the exponent. Scaling of the surface tension with the droplet size of the form $\sigma(\xi) \propto \xi^{-1/2}$ results in the Adam-Gibbs law for the relaxation time, which, in this concept, corresponds to the time of creating a mobile region rich in configurational entropy. This picture, however, does not directly address the question of the origin of viscous flow assuming that the mosaic structure of the dynamically exchanging mobile and immobile regions will have all the properties necessary to facilitate shear relaxation. The divergent length-scale of mosaic regions scales as\textsuperscript{23}

$$\xi \propto S_c(T)^{-2/3}$$ in contrast to $S_c(T)^{-1}$ scaling in the Adam-Gibbs theory.

The Adam-Gibbs relation can be tested by calorimetry\textsuperscript{20,27} or by using relaxation times and configurational entropies from computer experiments.\textsuperscript{28,29,30,31,32,33,34} In the former case, one has to assume that $S_c$ can be approximated by the excess entropy of a liquid over the crystal $S^{ex}$, although this is known to be a poor approximation in many cases.\textsuperscript{35,36,37,38,39} Nevertheless, the Adam-Gibbs equation is known to work well for both $S^{ex}$ and $S_c$, although it does not produce perfectly straight lines for $\ln(\tau)$ vs $1/T S^{ex}$, in particular for fragile liquids. The use of $S^{ex}$ in the Adam-Gibbs equation generally fails above the temperature $T_g$ at which the dynamics change character (e.g. bifurcation into $\alpha$ and $\beta$ processes).\textsuperscript{27}

The Adam-Gibbs equation with $S^{ex}$ used for $S_c$ is often equivalent to the VFT equation because many glass-formers\textsuperscript{27,40} empirically follow the $1/T$ entropy decay:

$$S^{ex}(T) = S_0 (1 - T^{ex}/T),$$ (6)

where $T^{ex}$ is what we will call the experimental Kauzmann temperature obtained by extrapolating $S^{ex}(T)$ to zero, in contrast to the thermodynamic Kauzmann temperature $T_K$ defined by Eq. 4. Equation 6 often applies to configurational entropies obtained from simulations, although bilinear in $1/T$ forms have also been used to fit the data.\textsuperscript{41,42}

A strong experimental argument in favor of the Adams-Gibbs picture is the near equality\textsuperscript{28} of the Kauzmann temperature $T_K^{exp}$ and the VFT temperature $T_0$. Further evidence is provided by the good account it gives of the pressure dependence of the glass transition temperature.\textsuperscript{43,44,45} However, the theoretical relevance of the concept of nucleation of cooperatively rearranging regions is not clear. Given the fact that laboratory glass-formers and model fluids equilibrated at higher temperatures in computer experiment approximately follow Eq. (6), one wonders to what extent the combination of Eqs. 3 and 6 is just a successful mathematical relation, reproducing the VFT law in Eq. (2), and whether activated events in supercooled liquids are really driven by the entropy. The resolution of this problem is important from a general perspective since the Adam-Gibbs picture puts supercooled liquids in a unique position within the more general problem of activated events in condensed matter. For most cases, including the vast majority of chemical reactions, excess kinetic energy at a transforming unit or a molecular mode, and not the entropy, is the driving force which lifts the system to the top of the activation barrier. This, more traditional, view of relaxation of supercooled liquids is advocated by models that consider kinetic energy or enthalpy as the driving force of activated transitions.\textsuperscript{41,45}

In models of activation controlled by the kinetic energy, one considers excitations to a common high-energy level above the “top” of the landscape corresponding to high-temperature diffusion.\textsuperscript{46} The energy of the starting point at a basin minimum is treated as a random variable within trap models\textsuperscript{47,48} or random-walk models.\textsuperscript{49,51,52} All such models result in activated kinetics with a temperature-dependent activation energy. However, since the probability of transition is finite at each temperature, no divergent relaxation time appears in these models.

A potential advantage of the energy models is the opportunity to unite the thermodynamics and dynamics of supercooled liquids within one conceptual framework, and this is the motivation of the present paper.
In the past, the two-state model by Angell and Rao\textsuperscript{33} led to configurational entropies that are in quite good agreement with experimental data.\textsuperscript{54} The model suggests that the thermodynamics of super-cooled liquids can be described by an ensemble of non-interacting two-state excitations, each creating an excess of entropy.\textsuperscript{56} A recent extension of the model\textsuperscript{53} considered two Gaussian manifolds of levels (2G model) instead of two discrete states of the original two-state model. This variant of the random energy model, conceptually related to Bässler’s random-walk picture,\textsuperscript{50,51} allowed an accurate fit of the laboratory and simulation data for heat capacities and configurational entropies. Here, we present a somewhat simplified version of this model that considers excitations from the single-energy level of the ideal glass to a Gaussian manifold of configurationally excited states (1G model). The thermodynamic analysis is then further used as a basis for a dynamic model of configurational excitations.

Our model of dynamics of viscous liquids follows the philosophy of the energy models of activation in that it considers the probability of accumulating kinetic energy sufficient to lift a “structural element” (or “excitable unit”), see Fig. 1, to an energy level corresponding to the activated state of the high-temperature relaxation. The kinetic energy supplied by the surroundings of a given excitable unit is a fluctuating variable with a fluctuation width related to the ruggedness of the landscape through the configurational heat capacity. The average of the fluctuations of the kinetic energy results in a relation for the relaxation time which gives an increase of the activation energy with decreasing temperature in terms of the configurational heat capacity, rather than the configurational entropy of the Adam-Gibbs theory. The new relation gives an account of experimental dielectric relaxation comparable to the Adam-Gibbs formula, but more acceptable in several ways to be discussed below.

II. THERMODYNAMICS OF CONFIGURATIONAL EXCITATIONS

A. Formulation of the model

We conceive an excitation\textsuperscript{53,54,57} to be a local increase in potential energy that results from a collisional redistribution of kinetic energy amongst some minimum group of “rearrangeable units” of the liquid structure. In this redistribution a “unit” (Fig. 1) that undergoes an excessively anharmonic vibrational displacement can get trapped by the motions of neighbors that act to prevent a return of the unit to its original center of oscillation, such that some kinetic energy will be lost from the vibrational manifold and stored in the configurational manifold. It is the constant and repeated exchange of energy between these manifolds that is the essence of configurational equilibration. The ability to store potential energy by this mechanism determines the configurational heat capacity.

The mathematical realization of this concept assumes that a liquid can be divided in real space into excitable units that follow the statistics of independent entities. Since these units form a continuous dense liquid phase and should be interacting, their actual interactions are represented by mean-field parameters of excitation energy $\epsilon_0$, excess entropy $s_0$, and excess volume $v_0$. Each excitable unit is a truly microscopic object as small as a fragment of a molecule or a single chemical bond of a network glass. The low-energy state is identified with the ideal glass, while excitations associated with molecular motions belong to a Gaussian manifold of energies with the width $\sigma$ (Fig. 2). The energetic disorder arises from the local disordering field and packing restrictions around a given excitable unit.

The real-space model of two-state excitations is next projected onto Goldstein’s configuration space of a liquid at constant pressure.\textsuperscript{22} This configuration space can be separated into basins of attraction characterized by the minimum depth $\phi$. We can write the excess Gibbs energy relative to the energy of the ideal-glass state (superscript “ex”) as a double sum over the basin energies and the fraction of excited units $x$ out of $N$ excitable units:

$$ e^{-\gamma x N/T} = \sum_{\phi} e^{-\phi N/T} \sum_{0 \leq x \leq 1} e^{\phi(x)} \tag{7} $$

where

$$ e^{\phi(x)} = \frac{N!}{(N-xN)!xN!} [(Q_0^e/Q_0^g)^x P(\phi, x)]^N \tag{8} $$

Here, $P(\phi, x)$ is the distribution of minimum energies in configuration space obtained by projecting the excitation energy $x(\epsilon_0 + PV_0 + \delta \epsilon)$ on the Gaussian manifold

$$ P(\phi, x) = \int \delta(\phi - x(\epsilon_0 + PV_0 + \delta \epsilon)) G(\delta \epsilon) d\delta \epsilon \tag{9} $$

where $G(\delta \epsilon)$ is a Gaussian distribution

$$ G(\delta \epsilon) \propto \exp \left[ -\frac{(\delta \epsilon)^2}{2\sigma^2} \right] \tag{10} $$
 FIG. 2: Configurational excitations and flow/relaxation events in the 1G model. The thermodynamics of supercooled liquids is represented in real space by excitations from a single energy level of the ideal glass into a Gaussian manifold of configurationally excited states. Each excitation lifts the energy of an excitable unit [Fig. 1] by energy $e_0(x)$ [Eq. (12)] and entropy $s_0$. The distribution of these states is much broader for fragile liquids than for intermediate and strong liquids. Relaxation is described by the dynamics of activated transitions in configuration space from basin minima of configurationally excited states to a common energy level $e_D$ above the top of the energy landscape. The activation barrier $e_D + \Delta \phi$ is a sum of the high-temperature activation energy $e_D$ and the difference $\Delta \phi$ of the average energy of the basin minima from the high-temperature plateau.

All energies here and below are in K, entropies and heat capacities are in units of K$_T$.

The ratio of vibrational-rotational partition functions $Q_v^g/Q_v^e$ in the ground (superscript “g”) and excited (superscript “e”) states can be absorbed into the excitation entropy

$$s_0 = \ln [Q_v^g/Q_v^e] = s_0^g + s_0^e$$

(11)

which is composed of the harmonic vibrational contribution, $s_0^g$, and a configurational contribution, $s_0^e$. The vibrational excitation entropy is related to the excess density of states of low-frequency vibrational modes near and below the boson peak

$$s_0^e = \sum_{\omega} (g_v^e - g_v^g) \ln [\omega].$$

(12)

In Eq. (12), the sum runs over the vibrational frequencies $\omega$ (eigenvalues of the Hessian matrix) with the densities of vibrational states in the ground and excited states $g_v^g$.

The thermodynamic limit $N \to \infty$ transforms the entropy $s(\phi, x)$ in Eq. (17) into a sum of the ideal mixing entropy, $s_0(x)$, and a Gaussian term

$$s(\phi, x) = s_0(x) - \frac{[\phi - x(e_0 + P\nu_0)]^2}{2\sigma^2},$$

(13)

where

$$s_0(x) = x s_0 - x \ln(x) - (1 - x) \ln(1 - x).$$

(14)

The sum over $x$ in Eq. (11) is determined by its largest summand at $x = x(\phi)$. One then arrives at the landscape thermodynamics in which the thermodynamic observables are determined by the excess free energy function depending on $\phi$ (we omit the dependence on $P$ for brevity)

$$g^{ex}(\phi) = \phi + e^{ex}_{anh}(\phi) - T s^{ex}(\phi),$$

$$s^{ex}(\phi) = s(\phi, x(\phi)),$$

(15)

where $e^{ex}_{anh}(\phi)$ is the energy related to the anharmonicity effects not included in the harmonic approximation (entropy from anharmonicity is small as indicated by computer simulations). The excess free energy $g^{ex}(\phi)$ is composed of the configurational and vibrational parts

$$g^{ex}(\phi) = g_v(\phi) + g_c(\phi),$$

(16)

where

$$g_v(\phi) = e^{ex}_{anh}(\phi) - x(\phi)s_0^v T.$$  

(17)

One can alternatively consider the sum over $\phi$ that maximizes at the average basin energy $\langle \phi(x) \rangle$. The (partial) Gibbs energy can be considered as a function of the population:

$$g^{ex}(x) = \langle \phi(x) \rangle + e^{ex}_{anh}(\langle \phi(x) \rangle) - T s(\langle \phi(x) \rangle, x).$$

(18)

The minimum of $g^{ex}(x)$ gives the thermodynamic Gibbs energy $g^{ex}$ in Eq. (7). The formulation in terms of $g^{ex}(x)$ is thermodynamically equivalent to the landscape thermodynamics in terms of $g^{ex}(\phi)$ since the thermodynamic Gibbs energy $g^{ex}$ is achieved at the largest summand in both $x$ and $\phi$ in the double sum in Eq. (7). We will, however, obtain both $g^{ex}(\phi)$ and $g^{ex}(x)$ in order to gain better insight into the physics of the model.

The excitation energy $e_0$ can, to the first approximation, be considered as independent of temperature. The situation is quite different with the Gaussian width $\sigma^2$. The energy of the localized excited state is randomized by interactions with the thermal motions of the liquid which are not quenched and therefore affected by temperature. The fluctuation-dissipation theorem then requires that $\sigma^2 = 2\lambda T$ scales linearly with temperature, as does the mean-square displacement of a classical harmonic oscillator, $\langle x^2 \rangle \propto T$. Here, $\lambda$ is the trapping energy or the energy of stabilization of an excitation by the difference $\Delta \phi$ of the average energy of the basin minima from the high-temperature plateau.
central components of the present model. The energy landscape of the system, i.e. energy as a function of 3N coordinates of the molecules making up the liquid, is determined by intermolecular interactions and is expected to be weakly temperature dependent at constant volume of the liquid. However, when the manifold of all possible states in 3N-space is projected onto one single coordinate of the basin energy \( \phi \), the distribution of \( \phi \), given in terms of the (partial) free energy \( g^{\text{ex}}(\phi) \), gains temperature dependence. Not only the first moment of this distribution, the average basin energy, is temperature dependent, as indeed described by random-energy models but essentially all higher moments are temperature-dependent as well. The random-energy model, originally developed for spin glasses, assumes that the width of the Gaussian distribution of random spin configurations is independent of temperature. This assumption is well justified for systems with quenched disorder, but probably not as well for liquids in a metastable (slow nucleation) equilibrium. Likewise the original Stillinger-Weber formulation assumed that temperature affects only the average energy \( \langle \phi \rangle \) in the form of “descending into the landscape” but not any higher moments of the distribution. The simulation evidence on this matter is insufficient and somewhat controversial. While some simulations of small ensembles of binary Lennard-Jones (LJ) fluids give clear indication of an approximately linear dependence of \( \langle (\delta \phi)^2 \rangle \) on \( T \), simulations of larger systems give virtually constant width. This distinction is not accidental. The width of the distribution of inherent structures scales as \( 1/\sqrt{N} \) and needs to be measured on small ensembles.

The ideal-glass state should in principle involve randomness (simulations for network liquids show a finite configurational entropy at the cutoff energy) and the previous version of the model (2G model) assumed Gaussian distributions for both the ideal glass energies and the excited configurations with the widths \( \sigma_i^2 = 2k_\text{B}T \lambda_i \) \((i = 1, 2)\). However, as we noted in Ref.\(^{57}\), the fit of the 2G model to experimental heat capacities and configurational entropies resulted in a small and almost constant \( \lambda_1 \approx 15 - 40 \) K for the ideal-glass state. The application of the model to a more extensive list of glass-forming liquids performed in this paper has shown that \( \lambda_1 \) can be set equal to zero without sacrificing the quality of the fit. This will be the model adopted here. This version of the model, with only one Gaussian manifold for the configurationally excited states, will be referred to as the 1G model. The random energy statistics we consider here have much in common with the model of protein folding proposed by Bryngelson and Wolynes and the equations we derive share features with the earlier cooperative two-state model of Strässler and Kitto (which is a forerunner of the two species non-ideal liquid model of Rapoport, the “two liquids” model of Aptekar and Ponyatovsky and co-workers and the cooperative defects models of Granato and of Angell-Moynihan).

Now we turn to the thermodynamics of configurational excitations. The excess Gibbs energy \( g^{\text{ex}}(\phi) \) minimizes at the average basin energy

\[
\langle \phi \rangle = x(\epsilon_0 + P v_0) - 2x^2\lambda(1 + \partial \epsilon^{\text{ex}}_{\text{anh}}/\partial \phi).
\]

In what follows we will neglect the generally unknown derivative \( \partial \epsilon^{\text{ex}}_{\text{anh}}/\partial \phi \). This approximation is expected to be accurate at low temperatures close to \( T_g \), but will fail at higher temperatures above the onset temperature at which the system starts to descent into the energy landscape. In this approximation, the excited-state population is defined by the self-consistent equation

\[
x = \left[ 1 + e^{\phi_0(x)/T} \right]^{-1},
\]

where the free energy per excitable unit is

\[
g_0(x) = \epsilon_0(x) + P v_0 - T s_0.
\]

Because of the energetic disorder of the exited states the actual excitation energy is lowered by twice the trapping energy \( 2\lambda \). However, only configurationally excited states can “solute” (stabilize) the excitation, and the stabilization energy is proportional to the population \( x \) of the excited states. The effective excitation energy \( \epsilon_0(x) \) in Eq. \( 21 \) and Fig. 2 then becomes

\[
\epsilon_0(x) = \epsilon_0 + P v_0 - 2x\lambda,
\]

where the factor of two comes from counting all interactions of a given unit with the rest of the ensemble of configurational excitations.

By relating \( x \) to the spin variable \( \sigma = 2x - 1 \) Eq. \( 20 \) can be brought to the form usually considered by models of ferromagnetism.

\[
\sigma = \tanh \left[ \frac{\lambda\sigma}{2T} - \frac{g_0 - \lambda}{2T} \right],
\]

where the excess Gibbs energy of configurational excitations is

\[
g_0 = \epsilon_0 + P v_0 - T s_0.
\]

At \( s_0 = 0 \) and \( \lambda = \epsilon_0 + P v_0 \) Eq. \( 20 \) transforms into the Weiss formula for spontaneous magnetization with \( \lambda\sigma/2 \) playing the role of the effective field of the magnetic moments.

The self-consistent equation for the population of configurationally excitation [Eq. \( 20 \)] bears some similarity with the results of previous studies minimizing the mean-field free-energy functionals of liquid-state theories. The density of the liquid \( \rho(x) \) can then be found from the self-consistent equation

\[
\rho(r) = q \exp \left( \int c(r - r') \rho(r') dr' \right),
\]

where \( q \) is the activity and \( c(x) \) is the direct correlation function.
the thermodynamic transition is reached, in qualitative agreement with our analysis of experimental data (see below).

The combination of the average energy [Eq. (19)] and excess entropy [Eqs. (13) and (15)] as functions of population yields $g^x(x)$ in Eq. (18)

\[
g^x(x) = x g_0 - x^2 \lambda + e^{s_x}_{\text{anh}} (\phi(x)) + T [x \ln x + (1-x) \ln(1-x)].
\] (26)

Except for the anharmonic correction, this equation has been derived in many previous publications.\textsuperscript{22,23,74,75,83} Minimization of $g^x(x)$ with respect to $x$ (neglecting the derivative $\partial e^{s_x}_{\text{anh}} / \partial x$) leads to Eq. (20). The parameter $\lambda$ then plays the role of the average energy of interaction between the configurational excitations. Consequently, the quadratic in $x$ term in Eqs. (19) and (20), originating from the energy randomness in our model, is equivalent to direct mean-field (Bragg-Williams)\textsuperscript{24} interaction between the excited units. In other words, randomness is effectively equivalent to attraction when separate units independently seek the same satisfactory configuration.\textsuperscript{75} Notice that derivation of Eq. (20) requires the explicit account of the linear temperature scaling of the real-space Gaussian width $\sigma^2$ in Eq. (10). The assumption of a temperature-independent width would result in a $1/T$ scaling of the energy term in $g^x(x)$ quadratic in $x$.

Since the full calculation of the excess thermodynamics of the supercooled liquid over its crystal is too a complex task even for phenomenological models we next assume that the excess entropy of configurational excitations over the ideal-glass state, $s^x(T)$, gives the excess entropy of the liquid over its crystal. We will use this excess entropy for the rest of our thermodynamic analysis warning at this point that this entropy is not thermodynamically consistent with the excess Gibbs energies in Eqs. (15) and (20), i.e. $s^x(T) \neq - (\partial g^x(T) / \partial T)_p$. A thermodynamically consistent $g^x(T)$ can of course be obtained by temperature integration of $s^x(T)$.

According to our derivation above, $s^x(T)$ is the sum of the configurational entropy $s_c(T)$ and the vibrational entropy $x(T)s_0^c$:

\[
s^x(T) = s_c(x(T)), T) + x(T)s_0^c,
\] (27)

where $\langle \phi(x(T)) \rangle$ and $x(T)$ are given by Eqs. (19) and (20), respectively. The configurational entropy thus accommodates only that part of $s_0$ which is not related to the change in the vibrational density of states. It is given as a sum of the ideal mixture entropy $s_0^c(x)$ and the fluctuation entropy $-x^2 \lambda / T$ consequent on the shrinking of the Gaussian width with decreasing temperature.\textsuperscript{27}

\[
s_c(x(T)) = s_0^c(x) - x^2 \lambda / T,
\] (28)

where

\[
s_0^c(x) = x s_0^c - x \ln x - (1-x) \ln(1-x).
\] (29)

B. Application to experimental data

We now proceed to applying the model to laboratory and simulation data for supercooled molecular liquids. In the former case, excess entropy $\Delta s$ of the liquid over the ideal-glass state $s^x(T)$ [Eq. (27)]. In the case of simulations, conjugate gradient minimization of simulated trajectories allows sampling of inherent structures, and equations for the configurational component of the excess entropy will be used [Eqs. (28) and (29)]. The two

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**TABLE I: Number of excitable units ("beads") per mole of a glass-former. The last column represents the effective number of classical oscillators in a molecule (mole) of a substance at $T_0$.**

| Substance       | Privalko\textsuperscript{24} | Takeda\textsuperscript{25} | Moynihan\textsuperscript{26} | Stevenson\textsuperscript{25} | $C^\alpha_{(T)}(T_0)/3$ |
|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------|
| Inorganics      |                             |                             |                             |                             |                        |
| Se              | 1                           | 1                           | 1                           | 0.9                         | 1                      |
| ZnCl\textsubscript{2} | 1                           |                             |                             |                             |                        |
| Aromatics       |                             |                             |                             |                             |                        |
| Toluene         | 4                           | 1                           | 2.7                         | 3.2                         |
| o-terphenyl (OTP) | 9                           | 2                           | 3.7                         | 3.2                         |
| Paraffinics     |                             |                             |                             |                             |                        |
| 2-methylpentane | 6                           | 3                           | 3.8                         | 3.2                         |
| Alcohols        |                             |                             |                             |                             |                        |
| Methanol        | 2                           | 2                           | 1.3                         | 1.76                        |
| Glycerol        | 6                           | 6                           | 4.5                         | 3.5                         |
| Hydrates        |                             |                             |                             |                             |                        |
| Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O | 13                          |                             | 7.0                         | 11.7                        |

Notice that derivation of Eq. (26) requires the explicit account of the linear temperature scaling of the real-space Gaussian width $\sigma^2$ in Eq. (10). The assumption of a temperature-independent width would result in a $1/T$ scaling of the energy term in $g^x(x)$ quadratic in $x$. Since the full calculation of the excess thermodynamics of the supercooled liquid over its crystal is too a complex task even for phenomenological models we next assume that the excess entropy of configurational excitations over the ideal-glass state, $s^x(T)$, gives the excess entropy of the liquid over its crystal. We will use this excess entropy for the rest of our thermodynamic analysis warning at this point that this entropy is not thermodynamically consistent with the excess Gibbs energies in Eqs. (15) and (20), i.e. $s^x(T) \neq - (\partial g^x(T) / \partial T)_p$. A thermodynamically consistent $g^x(T)$ can of course be obtained by temperature integration of $s^x(T)$.

According to our derivation above, $s^x(T)$ is the sum of the configurational entropy $s_c(T)$ and the vibrational entropy $x(T)s_0^c$:

\[
s^x(T) = s_c(x(T)), T) + x(T)s_0^c,
\] (27)

where $\langle \phi(x(T)) \rangle$ and $x(T)$ are given by Eqs. (19) and (20), respectively. The configurational entropy thus accommodates only that part of $s_0$ which is not related to the change in the vibrational density of states. It is given as a sum of the ideal mixture entropy $s_0^c(x)$ and the fluctuation entropy $-x^2 \lambda / T$ consequent on the shrinking of the Gaussian width with decreasing temperature.\textsuperscript{27}

\[
s_c(x(T)) = s_0^c(x) - x^2 \lambda / T,
\] (28)

where

\[
s_0^c(x) = x s_0^c - x \ln x - (1-x) \ln(1-x).
\] (29)
TABLE II: Best-fit parameters of the 1G model to experimental excess entropies and heat capacities. Also shown are the experimental Kauzmann temperature $T_K^{\exp}$ obtained by extrapolating experimental entropies to zero (Ref. 54) and by using Eq. 35, experimental VFT temperature $T_o$, and the thermodynamic Kauzmann temperature $T_K$ calculated from Eq. 36 using the 1G excess entropy from Eqs. 27–29. The temperature of liquid-liquid transition $T_{LL}$ is calculated from Eq. 34, $T_g$ is the experimental glass transition temperature. All energies and temperatures are in K, the entropy $s_0$ is in k$_B$ units.

| Substance                | $m$ | $z$ | $c_0$ | $\lambda$ | $s_0$ | $T_K^{\exp}$ | $T_o$ | $T_K^{\exp}$ | $T_{LL}$ | $T_K$ | $T_g$ |
|--------------------------|-----|-----|-------|-----------|-------|---------------|-------|---------------|----------|-------|-------|
| Toluene                  | 105 | 1   | 2171  | 1020      | 10.2  | 100           | 96.5  | 100           | 113      | 108   | 117   |
| D,L-propene carbonate (PC)| 104 | 1   | 2921  | 1383      | 10.7  | 129           | 129   | 144           | 123      | 156   |       |
| o-terphenyl (OTP)        | 81  | 2   | 3576  | 1686      | 8.3   | 204           | 202.4 | 206           | 228      | 170   | 246   |
| 2-methyltetrahydrofuran (MTHF) | 65  | 2   | 899   | 414       | 5.9   | 69            | 70    | 82            | 50       | 91    |       |
| Salol                    | 63  | 3   | 2070  | 988       | 5.6   | 175           | 175   | 176           | 193      | 115   | 220   |
| 3-bromopentane (3BP)     | 53  | 4   | 348   | 20        | 2.0   | 84            | 83    | 75            | 108      |       |       |
| Glycerol                 | 53  | 7   | 738   | 5.0       | 1.6   | 137           | 130   | 59            | 190      |       |       |
| n-propanol (nPOH)        | 35  | 2   | 406   | 22        | 2.8   | 72            | 70    | 30            | 96       |       |       |

$^a$Steepness fragility index, Eq. 33.
$^b$Taken from Ref. 27 unless indicated otherwise.
$^c$From Ref. 35.
$^d$Calculated from Eq. 35.
$^e$Obtained as the temperature of crossing zero for the excess entropy calculated in the 1G model.

The separation of a molecule into $z$ statistically independent subunits neglects the finite correlation length of the disordering field. Indeed, if two units are within the field’s correlation length, they contribute to the statistics of basins as a single unit. The number of units $z$ is thus an effective parameter necessarily smaller or equal to the number of conformationally distinct units (cf. the difference between Privalko’s conformational and Stevenson’s effective numbers in Table II). Because of its effective nature, $z$ can be represented by fractional numbers as was done by Stevenson and Wolynes (Table II). Although this approach provides more flexibility in fitting the experiment, we will follow here Takeda et al. 84 and Moynihan and Angell’s estimates were based on best fitting of the excess entropy to an excitations model. Some comparisons are provided in Table II.

We will apply the model to constant-pressure data and consider the excitation energy $c_0$ as an adjustable parameter. Therefore, for the rest of our analysis, the term $Pv_0$ in the excess Gibbs energy [Eq. 24] is fused into...
\(\epsilon_0\). Therefore, given the number of excitable units per molecule \(z\) has been specified, the 1G model contains three model parameters, \(\epsilon_0\), \(\lambda\), and \(s_0\). We have tested the model for a set of glass-formers identified as fragile (strong super-Arrhenius kinetics, from toluene to salol) and intermediate (weak super-Arrhenius kinetics, from 3-bromopentane to \(n\)-propanol) liquids. Results shown in Fig. 3 and listed in Table I were obtained from a simultaneous fit of the model to excess heat capacities and entropies from Ref. 54, bound by the constraint \(\epsilon_0(x) \geq 0\) [Eq. (22)] required for the mechanical stability of the ideal-glass state.

The experimental excess entropies are calculated from the constant-pressure heat capacity \(C_P^{\text{ex}}(T)\) and the fusion entropy \(\Delta S_{\text{ fus}}\) according to the relation

\[
S^{\text{ex}}(T) = \Delta S_{\text{fus}} + \int_{T_{\text{fus}}}^{T} C_P^{\text{ex}}(T') (dT'/T'),
\]

where \(T_{\text{fus}}\) is the fusion temperature and \(S^{\text{ex}}(T) = zS^{\text{ex}}(T)\). The number of excitable units per molecule (mole) \(z\) was taken from Moynihan and Angel24 and varied additionally to find the best-fit integral numbers. Equal quality fits can be obtained in some cases with varied additionally to find the best-fit integral numbers. Equal quality fits can be obtained in some cases with different numbers \(z\), e.g. for toluene \(z = 1\) and \(z = 2\) can be adopted. In that latter case, \(z = 1\) was taken to maintain the consistency of parameter values with other fragile liquids (Table I). The choice of \(z\) here does not affect our qualitative conclusions discussed below.

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At \(\lambda = 0\) this equation reduces to Schottky’s heat capacity \(C_P^{\text{ex}} = x(1 - x)(\epsilon_0(T)/T)^2\), which is further reduced to the Hirai-Eyring equation95 proposed on the basis of transition-state ideas, in the limit \(x \ll 1\). For fragile liquids, \(x \simeq 1\), as we show below, and the heat capacity becomes:

\[
c_P^{\text{ex}} = \frac{\lambda}{T}.
\]

Notice that Eq. (31) anticipates a Curie-type, \((T - T_c)^{-1}\), divergence of the heat capacity at the critical temperature defined by the equation \(T_c = 2\lambda x(T_c)(1 - x(T_c))\).

The fragility of a glass-former is often characterized by the steepness index\(22\)

\[
m = \frac{d \log \tau}{dT} |_{T = T_g}
\]

(listed in Table I) or by its thermodynamic equivalent\(22,24\). What appears to be a smooth transition from fragile salol to intermediate 3-bromobenzene according to the steepness index in fact corresponds to a drastic decrease in the trapping energy by a factor of about 50. Low values of \(\lambda\) turn out to be characteristic of all intermediate liquids in Table I. The result is a profound change in the relative importance of the ideal mixing and Gaussian terms in the excess entropy.

For fragile liquids, the ideal mixing entropy constrained by the assumption that the trapping energy \(\lambda\) is independent of temperature. This assumption is supported by spectroscopic studies showing weak dependence of the Stokes shift (which is an analog of the trapping energy for electronic transitions) on temperature.\(90,91\) With this assumption one gets:

\[
c_P^{\text{ex}} = \frac{\epsilon(x)(1 - x)(2\lambda_x)}{2(1 - x(1 - x)(2\lambda_x/T))}.
\]

At \(\lambda = 0\) this equation reduces to Schottky’s heat capacity \(C_P^{\text{ex}} = x(1 - x)(\epsilon_0(T)/T)^2\), which is further reduced to the Hirai-Eyring equation proposed on the basis of transition-state ideas, in the limit \(x \ll 1\). For fragile liquids, \(x \simeq 1\), as we show below, and the heat capacity becomes:

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Notice that Eq. (31) anticipates a Curie-type, \((T - T_c)^{-1}\), divergence of the heat capacity at the critical temperature defined by the equation \(T_c = 2\lambda x(T_c)(1 - x(T_c))\).
However, when this restriction is imposed on the parameters, the model fails to fit the experimental data.

The physics is quite different for intermediate liquids for which the ideal mixture term provides the main part of $s_{\text{ex}}(T)$. The excess entropy then decreases with temperature due to decreasing population of the excited state, which cannot stay at a high value because of a smaller entropy gain $s_0$ compared to fragile liquids (glycerol in Fig. 4). The entropy smoothly decreases without a discontinuity related to thermodynamic phase transition (see Fig. 5 for the illustration of various temperatures used in the present thermodynamic analysis).

The disappearance of the first-order transition for non-fragile (strong and intermediate) liquids is related to two critical parameters, critical temperature $T_c$ and critical excitation entropy, $s_{0c}$. A first-order phase transition is possible for temperatures below $T_c$ and entropies higher than $s_{0c}$.

$$T < T_c, \quad s_0 > s_{0c},$$

where

$$T_c = \lambda / 2, \quad s_{0c} = 2s_0 - \lambda - 2.$$  

At least one of two inequalities in Eq. (36) is violated for non-fragile liquids as a result of low excitation entropies $s_0$ and trapping energies $\lambda$.

In parallel to the excess entropy, the average basin energy $\langle \phi \rangle$ shows qualitatively different temperature behavior for fragile and intermediate liquids. With temperature decreasing, $\langle \phi \rangle$ from Eq. (19) starts to dip as $1/T$ from a high-temperature plateau and then inflects into an exponential temperature dependence $\exp(-\epsilon_0/T)$ for $\epsilon(x)/T \gg s_0$. Both the $1/T$ decay at relatively high temperatures and exponential decay at low temperatures (for a model network fluid) have been observed in simulations. In our model, this pattern describes non-fragile liquids. For fragile liquids, the excited state population is almost constant, $x \sim 1$, in the entire range of experimentally accessible temperatures down to the glass transition. The average basin energy is constant as well, $\langle \phi \rangle = \epsilon_0 - \lambda$. For infinitely slow cooling (and rare cases like triphenyl phosphite (TPP)), the population sharply changes at the liquid-liquid transition resulting in a discontinuous dip of the average energy $\langle \phi \rangle$ from its plateau value.

The temperature dependence of the excess entropy of fragile liquids above $T_g$ is mostly determined by the $1/T$ decay of the second, fluctuation term in Eq. (28). The result is the overall temperature dependence in the form of Eq. (30) with $S_0 = z s_0$. The experimental Kauzmann temperature $T_K$ is then obtained by extrapolating Eq. (12) to zero entropy, which leads, in terms of the model parameters, to the following relation

$$T_{K}^{\text{exp}} = \frac{\lambda}{s_0}. \quad \text{(38)}$$

Equation (38) holds quite well for the fit parameters in Table II. In addition, the constant-pressure heat capacity

\begin{figure}[h]
\centering
\includegraphics[width=0.7\linewidth]{figure5.png}
\caption{Temperature dependence of the average basin energy (a) and excess entropy (b) of fragile glass-formers. The almost flat dependence of the average energy on temperature is terminated by discontinuous first-order phase transition at temperature $T_{LL}$. At this temperature the excess entropy, as predicted by the 1G model [solid line in (b)], also shows a discontinuous drop to a nonzero value which decays to zero at the thermodynamic Kauzmann temperature $T_K$. The broken line in (b) illustrates the experimental interpolation of the high-temperature $1/T$ law ending up at the experimental Kauzmann temperature $T_{K}^{\text{exp}}$. The excess entropy is equal to the fusion entropy $\Delta S_{\text{fus}}$ at the melting temperature $T_m$. The dashed lines in (a) indicate the narrowing of the Gaussian distribution of excitation energies with decreasing temperature.}
\end{figure}
FIG. 6: Configurational entropy (a), configurational constant-volume heat capacity (b), and the fitted excitation parameters (c,d) for LW o-terphenyl (z = 2) is used as in the case of laboratory o-terphenyl, Table I. The points in (a) and (b) are the simulation data from Ref. 30 at the densities indicated in (c). The dotted lines in (c,d) connect the points. In (c), λ is indistinguishable from \( \varepsilon_0/2 \) on the scale of the plot for two lowest densities. The lines in (a) and (b) are simultaneous fits of the simulated configurational entropy and heat capacity to the 1G model; the dashed and dash-dotted lines are used for two lowest densities with high fragility to distinguish them from higher densities with intermediate fragility.

The fit of experimental data for fragile liquids shows that \( \varepsilon_0 \) is close to 2λ and in fact can be put equal to 2λ without sacrificing the accuracy of the fit. As a result, the thermodynamics of fragile liquids is defined by the following relations often used empirically:

\[
\begin{align*}
S^\text{ex}(T) & = c^\text{ex}_P(T_g)(T_g/T)^{\lambda} - \Delta S_{QA}(T_g), \\
c^\text{ex}_P(T) & = c^\text{ex}_P(T_g)(T_g/T).
\end{align*}
\]  

We note that random energy models, which do not anticipate temperature variation of the width of basin energy distribution, result in \( T^{-2} \) scaling of the heat capacity inconsistent with Eq. (40).

It is obviously significant for our discussion to compare the results of fitting the model to laboratory excess entropies with analogous fits to configurational entropies from simulations. The Lewis and Wahnström (LW) model of o-terphenyl studied in Refs. 20 and 31 provides us with such an opportunity. Figure 6 shows the fit of the 1G model to the configurational entropies and heat capacities of LW o-terphenyl at five different densities.

The number \( z = 2 \) is maintained equal to the analysis of experimental data to access the fraction of configurational excitation entropy in \( s_0 \). Two main results follow from the fit: (i) the 1G model predicts the existence of a critical \( \lambda \)-singularity below \( T_g \) for two lowest densities and its disappearance at higher densities, (ii) the configurational component of the excitation entropy following from the fit, \( s_0 \approx 2 \), is significantly lower than \( s_0 \approx 8 \) obtained for laboratory o-terphenyl (Table I). The appearance of the divergence at lower densities is the result of very close fulfillment of Eq. (39) for the fitting parameters, which is remarkable, given that the excitation parameters are freely varied in the fit. The magnitude of the fitted excitation entropy suggests that a major portion of \( s_0 \) arises from a change of the vibrational density of states as we have also learned from comparing the laboratory and simulation data for water (see below).

Our result is close to Goldstein’s estimate of 28% for the fraction of configurational component in the excess entropy of o-terphenyl. Goldstein’s calculation was based on the comparison of excess entropies of quenched and annealed glasses at \( T_g, \Delta S_{QA}(T_g) \), and at 0 K, \( \Delta S_{QA}(0) \). The ratio \( \Delta S_{QA}(0)/\Delta S_{QA}(T_g) \), which is equal to \( s_0^{\text{exp}}/s_0 \) in the 1G model, gives the configurational fraction of the excess entropy.

The fit of 1G thermodynamic model to experimental data (Table I) shows that the thermodynamic Kauzmann temperature \( T_K \) [Eq. (6)] is significantly lower than the experimental Kauzmann temperature \( T_K^{\text{exp}} \) [Eq. (6)]. This implies that the relaxation time in the Adam-Gibbs relation does not diverge at \( T_K^{\text{exp}} \approx T_0 \) and the link between the thermodynamics and dynamics might be more complex. The dynamic extension of the 1G model presented below places the emphasis on the configurational heat capacity, instead of the configurational entropy, as the main reason for super-Arrhenius dynamics in fragile liquids.

III. DYNAMICS OF CONFIGURATIONAL EXCITATIONS: ENTHALPIC DRIVING FORCE

A. Formulation of the model

Here we describe a dynamic model extending the thermodynamic analysis of Sec. II. Our development starts with the assumption common to all energy-trap9,49 and energy-diffusion50,51,52 models that non-reversible events of viscous flow and diffusion6 occur by exciting some states within the liquid to a common energy level \( E_0 \), which is higher than the top of the energy landscape61,68 (Fig. 2). These excitations occur by absorbing kinetic energy by an excitable unit (bead) from the surrounding liquid.

We will next assume that only unjammed configurationally excited units will participate in activated events. Even when a sufficient amount of energy has been accumulated at a given unit, relaxation event may require facilitation from other units. This is particularly clear in a case of a molecule composed of \( z \) units (beads). One could imagine that e.g. translational relaxation of such molecule would require excitation of all \( z \) units, although relaxation of conformationally flexible molecules can also proceed in a diffusive way, as a sequence of low-amplitude motions of consecutive units. Because of the assumed low amplitude of the motions involved, we will not distinguish between pairs of units within the molecule and pairs of units belonging to different molecules.
Each low-amplitude step is terminated by a transformation of the accumulated kinetic energy into a small structural change with a higher potential energy and thus higher fictive temperature. A single relaxation event requires a sequence of such locking steps by the end of which there appears a “hot” (in fictive temperature) region within the liquid which can then subsequently relax to a new configuration (Fig. 7). In this scheme the overall dynamics become hierarchical in character, the initial step being the most probable and hence the shortest in time. This picture is an integration of energy spikes seen in simulations of Heuer and co-workers\textsuperscript{99} with dynamical hierarchy of Palmer \textit{et al.}\textsuperscript{99} (see below).

The kinetic energy becomes increasingly scarce at low temperatures. The creation of a hot region will occur by pulling the kinetic energy from a growing number of neighboring molecules, leading to the creation of a hot island in a sea of kinetically frozen molecules (on the time scale of heat transport). This picture bears some similarity to the entropy-rich droplet enveloped by the entropy-frozen environment described by Lubchenko and Wolynes\textsuperscript{23} and by Bouchaud and Biroli\textsuperscript{23}. However, the notion of relaxation proceeding by occurrence of hot regions does not anticipate static, thermodynamically stable structures of the mosaic picture\textsuperscript{106} and instead corresponds to the idea of dynamic heterogeneity i.e. the existence of regions of markedly different mobility\textsuperscript{101,102} or in a dynamic fashion as facilitated kinetics of transfer of excitations from mobile particles to their neighbors\textsuperscript{55}. Our formulation will follow this latter pathway using the kinetic scheme of hierarchical relaxation events advanced by Palmer \textit{et al.}\textsuperscript{99}.

According to the hierarchically facilitated dynamics, step \(n+1\) happens only when a configuration at step \(n\) is reached to facilitate the next move\textsuperscript{99}. This idea has been instrumental in establishing the conceptual basis for kinetically constrained models\textsuperscript{106} and, physically, leads to dynamical heterogeneity when dynamically cooperative regions in the glass are created by a sequence of constrained motions of fastest molecules in the ensemble\textsuperscript{55}.

In our model, step \(n\) is reached when \(n\) excitable units within a hot island have “blinded” into the excited state with the probability

\[
P_n = \left(\frac{\tau_0}{\tau_1}\right)^n = \exp[\mu n],
\]

where \(\tau_1\) is the average waiting time for a single unit and \(\tau_0\) is the same as in Eq. (2). As a result of a sequence of correlated steps, each resulting in excitation of \(n\) units out of \(N_c\) units in the hot island, the waiting time of level \(n\) becomes\textsuperscript{99}

\[
\tau_n = \tau_0 \exp[\mu N_n]
\]

with \(N_n = n(n-1)/2\). We can now follow Brey and Prados\textsuperscript{107} to obtain the normalized relaxation function:

\[
\phi(t) = \zeta^{-1} \left[ E_1\left(\frac{t}{\tau_0}\zeta\right) - E_1\left(\frac{t}{\tau_0}\right) \right],
\]

where \(E_1(z)\) is the exponential integral function,

\[
\zeta = \mu N_{\max},
\]

and

\[
N_{\max} = N_c(N_c - 1)/2.
\]

For most practical purposes the relaxation function in Eq. (43) is indistinguishable (Fig. 8) from the KWW function in Eq. (1). In the intermediate range of times, \(1 \ll t/\tau_0 \ll e^\zeta\), which can be very broad since \(\zeta \gg 1\) for real systems, \(\phi(t)\) follows the logarithmic decay, \(\phi(t) \approx \ldots\)
The average relaxation time $\tau = \int_0^\infty \phi(t) \, dt$ from Eq. (43) is

$$\tau = (\tau_0/\zeta) \left( e^\zeta - 1 \right) \approx \tau_0 e^\zeta. \quad (46)$$

Notice that the KWW function is more flexible than Eq. (43) because it involves two free parameters, $\tau/\tau_0$ and $\beta$, in contrast to the single parameter $\zeta$ in Eq. (43). More complex facilitation rules than the ones used here will provide additional parameters and a possibility of realizing the KWW relaxation function, which has the advantage of allowing an approximate correlation between the stretch exponent and fragility.

Each elementary step within the hierarchal sequence requires overcoming the activation barrier between the average energy of the basin minimum $\langle \phi \rangle$ and the common energy level $E_0 = \zeta e_0$ (Fig. 9):

$$E_D(x) = E_D - \zeta \Delta \phi(x), \quad (47)$$

where $E_D$ is the activation barrier per molecule (mole) associated with the activated relaxation in the high-temperature liquid and

$$\Delta \phi(x) = (x - 1)e_0 - 2(x^2 - 1)\lambda \quad (48)$$

is the drop of the minimum energy from the high-temperature plateau below the onset temperature.

One can next assume that the kinetic energy necessary for activation is distributed in “quanta” of thermal kinetic energy $E_K = ze_K$ throughout the liquid, where $E_K$ and $e_K$ refer to a molecule (mole) and excitable unit, respectively. This physical picture seems appropriate for describing activated events in disordered materials since, according to theories of heat conductivity, the quasi-lattice vibrations in glasses are more appropriately described (in the temperature range above ca. 30 K) as quasi-localized vibrations rather than wave-like motions. The momentum exchange (heat transport) occurs by diffusional transport of vibrational energy by these quasi-localized modes in the vicinity of the boson peak. Activation of one unit then requires accumulating $m = E_D(x)/E_K$ “quanta” of kinetic energy, provided that that unit is not jammed being in the configurationally excited state. Therefore, the probability of activating one unit is equal to the probability of absorbing $m$ quanta of kinetic energy out of a manifold of $xN$ configurational excitations uniformly distributed over $N$ units (beads) in the liquid. This type of problem is considered in the theory of unimolecular bond dissociation. The solution by Kassel gives the probability of combining at least $m$ quanta of energy at one bond:

$$P_{\geq m} = \frac{(N + xN - m - 1)!(xN)!}{(xN - m)!(N + xN - m)!}. \quad (49)$$

For condensed-phase problems one takes the thermodynamic limit in the above equation, $N \to \infty$, with the result

$$P_{\geq m} = (1 + 1/x)^{-m} = \exp (-E(x)/E_K), \quad (50)$$

and $E_D(x)$ is given by Eq. (47). Because of similar combinatorial rules, not surprisingly, Eq. (50) is analogous to the equation for the probability of finding a hole with the volume exceeding some critical value $v^*$

$$P(v^*) = \exp (-\gamma v^*/v_f), \quad (52)$$

where $v_f$ is the free volume and $\gamma$ is a numerical coefficient. This equation is the key result of free-volume models of diffusion and relaxation in glass-formers.

The ideal glass transition is predicted to occur because the liquid is supposed to run out of free volume at a finite temperature. In contrast to that, the kinetic energy in Eq. (50) is a fluctuating variable which can approach zero for some basins in the distribution sampled at temperature $T$ ($\phi^{(3)}$ in Fig. 9), but whose average value is proportional to $T$.

The combinatorial arguments of the Kassel model envision the system as a microcanonical ensemble characterized by the average energy $\langle \epsilon \rangle$ uniformly distributed over the sample (Fig. 9). In order to apply these combinatorial rules to a macroscopic liquid, we need to use the microcanonical ensemble characterized by the average energy $\langle \epsilon \rangle$ analogously to the use of microcanonical ensemble to calculate the excess entropy in Eqs. (8) and (13). Since energy is an extensive variable, this description is equivalent in the thermodynamic limit to the canonical one in the sense that the fluctuations of the total energy can be neglected.

Each unit undergoing excitation to the common level $e_0$ by collecting kinetic energy from the surrounding molecules will find itself in a local disordering field characteristic of a particular basin of the rugged energy landscape (Fig. 9). The kinetic energy available to the surrounding molecules to excite a given molecule will be
a fluctuating variable producing disorder of $e_K$ which is quenched on the time-scale of momentum relaxation. The relaxation time of a single molecule $\tau_1$ then needs to be averaged over possible realizations of the kinetic energy

$$\tau_1 = \tau_0 e^{\mu} = \tau_0 \int \exp[E(x)/(ze_K)]P(e_K)de_K, \quad (53)$$

where $P(e_K)$ is the distribution of the kinetic energy.

For the energy landscape characteristic of strong and intermediate liquids the canonical narrow distribution of basin energies projects itself, in the microcanonical ensemble, into a narrow distribution of kinetic energy $e_K$. The distribution function $P(e_K)$ in Eq. (53) can be replaced by a delta function. Assuming that the average kinetic energy is equal to $E_K = (3/2)T$ (translations for diffusion and viscous flow and rotations for dielectric relaxation), and using Eq. (54) for $E(x)$ in Eq. (53) one gets for the average relaxation time

$$\ln(\tau/\tau_0) = (2/3T)(E_D - z\Delta\phi(x))\ln \left[2 + e^{(-s_0 + \epsilon(x)/T)}\right], \quad (54)$$

The relaxation is Arrhenius at high temperatures ($\epsilon(x)/T \ll s_0$ and $z\Delta\phi \ll E_D$). Two things happen when the temperature is lowered. First, the energy gap between the average minimum energy $\langle \phi_m \rangle$ and the energy level $\epsilon_0$ starts to increase as $a + b/T$ since $\Delta\phi(x)$ scales as $1/T$ right below the onset temperature. Second, at $\epsilon(x)/T > s_0$ the logarithmic term in Eq. (54) generates a $1/T$ factor. Overall, the temperature law at these low temperatures becomes

$$\ln(\tau/\tau_0) = E_1/T^2 + E_2/T^3, \quad (55)$$

which is a linear combination of the Bässler and Litovitz temperature laws.

This sort of non-Arrhenius kinetics is capable of describing the relaxation of intermediate liquids studied in Sec. II. Figure 10 shows experimental dielectric relaxation times vs the rhs of Eq. (54) calculated from the 1G model. The parameters affecting population $x$ are taken from our thermodynamic analysis summarized in Table II. Experimental high-temperature activation energies $E_D$ are from Ref. [114]. The analysis yields straight line with the slope 1.1 for n-propanol and a less clear linear trend for 3BP with the linear regression slope of 1.0. For glycerol, the slope of 1.0 is obtained by assuming the average kinetic energy equal to $3T$, which might reflect the participation of both rotational and translational degrees of freedom in the relaxation process. We need to note that vibrational heat capacity of many glass-forming liquids does not reach the Dulong and Petit limit in its low-temperature portion. Therefore, the average kinetic energy can fall below $(3/2)T$ also becoming a non-linear function of temperature. Accounting for this effect, which is not considered here, will make the temperature dependence in Eq. (54) even more complex.

Equation (55) is insufficient to account for super-Arrhenius behavior of fragile liquids from Table II. This is because fluctuations of the kinetic energy now need to be taken into account [Eq. (53)]. $E_K$ can be connected to the fluctuation of the energy of inherent structures by assuming that the average energy is $\langle E \rangle = (3/2)T + z\langle \phi \rangle$. The instantaneous kinetic energy is then

$$E_K = (3/2)T - z\phi,$$

where $\phi = - \langle \phi \rangle$. The distribution of $\phi$ is Gaussian,

$$P(\phi) = (2\pi c_p T^2)^{-1/2} \exp \left[-(\phi c_p T)^2/2\right]. \quad (57)$$

This follows from the bilinear expansion of the enumeration function $s^c(\phi)$ in $\phi$ and the use of two thermodynamic identities,

$$\langle \partial^2 s^c(\phi) / \partial^2 \phi \rangle_{N,P} = - (c_p T)^{-1},$$

where $c_p$ is the configurational heat capacity of the exciton [in contrast to the excess heat capacity in Eq. (57)]. Notice regarding Eq. (57) that Boltzmann statistics of the basin fluctuations follow from the hyperbolic, $c_p \propto 1/T$ scaling of the configurational heat capacity, while $1/T^2$ scaling of the random energy model leads to the temperature-independent statistics.

The average waiting time of a single molecule then incorporates the thermodynamic quantity, configurational heat capacity, into the kinetics through $P(\phi)$ in the integral:

$$\tau_1/\tau_0 = \int_{-\infty}^{3T/2z} \exp \left[\frac{E(x)}{3T/2 - z\phi}\right] P(\phi) d\phi. \quad (59)$$

A simple estimate of the integral in Eq. (59) can be obtained by linearly expanding the exponent in $\phi$, integrating over $\phi$, and reverting to the fractional form.

![FIG. 10: Test of Eq. (54) using dielectric relaxation data for intermediate liquids listed in Table II. The high-temperature activation energy $E_D$ in Eq. (54) is equal to 18.4$T_g$ (glycerol), 22.6$T_g$ (nPOH), and 16.0$T_g$ (3BP). $E_D$ for 3BP was obtained from its empirical connection to the steepness index $m$ given in Ref. [115]. The excited-state population $x(T)$ and $\Delta\phi(T)$ in Eq. (54) are calculated from the 1G model with the liquid parameters listed in Table II. The slopes of the linear regressions are 1.0 (glycerol), 1.1 (nPOH), and 1.0 (3BP), and the intercept gives the physical value of 10^{-13} s. In case of glycerol, the average kinetic energy of 3T has been adopted.](image-url)
TABLE III: Best-fit parameters of Eq. (61) to experimental dielectric relaxation data with $\tau_0$, $D$, and $T'$ considered as fitting parameters. The experimental (superscript “exp”) and calculate (superscript “calc”) pressure variation of the glass transition temperature $dT_g/dP$ is given in K/MPa, all temperatures are in K.

| Substance | $\log(\tau_0/s)$ | $D$ | $T'$ | $T'^a$ | $T'^b$ | $dT_g/dP^{exp}$ | $dT_g/dP^{calc}$ |
|-----------|-----------------|-----|-----|-------|-------|----------------|----------------|
| Toluene   | −15.6           | 145 | 9.3 | 9.8   | 8.7   | 0.26$^d$       | 0.22           |
| o-terphenyl (OTP)$^c$ | −14.0          | 161 | 13.8| 12.2  | 13.7  | 0.26$^d$       | 0.22           |
| 2-methyltetrahydrofuran (MTHF) | −13.5          | 95.6| 7.9 | 5.9   | 8.9   | 0.20$^c$       | 0.26           |
| Salol     | −14.4           | 204 | 11.9| 10.5  | 13.3  | 0.20$^c$       | 0.26           |
| 3-bromopentane (3BP) | −13.6          | 209 | 7.1 | 9.4   | 9.4   | 0.03$^f$       | 0.05$^g$       |
| Glycerol  | −14.2           | 159 | 13.2| 13.2  | 10.0  | 0.03$^f$       | 0.05$^g$       |
| n-propanol (nPOH) | −13.2          | 218 | 7.9 | 6.5   | 0.07$^b$ | 0.05$^i$       |

$^a$Calculated for fragile liquids from Eq. (65) by applying the thermodynamic fitting parameters from Table III.

$^b$Based on the steepness fragility index according to Eq. (65).

$^c$Fit to Eq. (61) for OTP was obtained by restricting $\log(\tau_0)$ to be equal to −14.

$^d$From Ref. 112.

$^e$From Ref. 111. The calculated $dT_g/dP$ refers to $P = 300$ MPa instead of atmospheric pressure in case of OTP since the data in Ref. 111 apply to high pressures only.

$^f$From Ref. 121.

$^g$Using high-temperature $T, P$-data for viscosity from Ref. 121.

$^h$Using high-temperature $T, P$-data for viscosity from Ref. 121.

$^i$Using the dielectric data at 0.1 MPa and 100 Mpa from Ref. 121.

Combining Eqs. (44), (40), and (59), the average relaxation time of the hot region is then obtained as

$$\ln (\tau/\tau_0) = \frac{2N_{max}E(x)}{3T - (4E(x)/9)zC_p(T)}, \quad (60)$$

where $N_{max}$ is given by Eq. (45) and the molecular (molar) configurational heat capacity $C_p(T)$ appears in the denominator. For fragile liquids, $E(x)$ is nearly independent of temperature down to the liquid-liquid transition point ($x \approx 1$, see Fig. 3) and can be considered as constant. This consideration yields the following equation for the relaxation time

$$\ln (\tau/\tau_0) = \frac{DT'}{T - T'C_p(T)}, \quad (61)$$

where the constant $D$ is

$$D = (9/4z)N_c(N_c - 1) \quad (62)$$

and the temperature $T'$ is described further below.

The parameters $D$ and $T'$ in Eq. (61) can be considered as empirical fitting quantities for the sake of interpreting the experiment. According to Eq. (32), the excess and configurational heat capacities of fragile liquids are equal to each other for fragile liquids. The $1/T$ scaling of the configurational heat capacity then results in the overall temperature dependence of the form

$$\ln (\tau/\tau_0) = \frac{DT'T}{T^2 - z\lambda T'}, \quad (63)$$

This type of the temperature law was obtained for hard-sphere fluids by Jagla$^{117}$ who combined the Adam-Gibbs formalism with an empirical equation of state. Note, however, that the configurational entropy in Jagla’s model has a $1/T^2$ temperature scaling inconsistent with the empirical $1/T$ law [Eqs. (6) and (40)].

### B. Application to experimental data

Equations (61) and (63) suggest some qualitative results consistent with experimental observations. First, the model establishes a direct link between fragility and configurational/excess heat capacity. The configurational heat capacity in the denominator of Eq. (61) decreases at high temperatures, e.g. above the melting temperature $T_m$. Therefore, the relaxation kinetics will change from super-Arrhenius at low temperatures to Arrhenius at high temperatures. The extent of fragile behavior is controlled by $\lambda$ in the denominator of Eq. (63) which, according to our thermodynamic analysis, is large for fragile liquids, resulting in curved Arrhenius plots. Note that parameter $D$ in Eqs. (61) and (63) is essentially constant across all liquids studied (Table III) in contrast to parameter $D$ in the VFT equation [Eqs. (2)] which correlates with fragility. Finally, Eq. (61) predicts a return to the Arrhenius behavior on passing below $T_g$ because of the drop of $C_p$ which defines $T_g$. This feature
fragile liquids. The nominator parameter $D$ in Eq. (61) can be related to the average number of excitations in the hot region via Eq. (59). However, the mathematical solution of the equation

$$T_0 = T' C_p(T_0)$$

(64)

can be associated with the VFT temperature $T_0$ often reported experimentally. The temperature $T_0$ calculated from this equation (Fig. 13) is almost equal to the experimental Kauzmann temperature $T_K$ for all liquids listed in Table III. Equation (61) is therefore consistent with the empirically documented accord between $T_0$ and $T_K$. For fragile liquids, Eq. (61) simplifies to [Eq. (52)],

has previously been unique to the Adam-Gibbs equation.

In addition to providing a qualitatively correct picture, Eq. (61) performs surprisingly well in fitting the dielectric relaxation times of both intermediate and fragile liquids (Fig. 11 and Table III), as well as of simulation data (see below). Fits of experimental dielectric relaxation times to Eq. (61), with $\tau_0$, $D$, and $T'$ considered as fitting parameters, are indistinguishable from VFT fits in all cases studied (Fig. 11 upper panel). $\ln(\tau)$ plotted against $DT/(T - T' C_p)$ also yields straight lines and physically reasonable intercepts (Fig. 11 lower panel). The quality of the linear correlations is as good as for the Adam-Gibbs plot (cf. Figs. 11 and 12) and in some cases is even better (MTHF). In all fits, experimental $C_p(T)$ were used instead of $C_p(T)$ suggested by the denominator of Eq. (61). In the 1G model, $C_p(T) \simeq C_p(T)$ for fragile liquids.

The nominator parameter $D$ in Eq. (61) can be related to the average number of excitations in the hot region via Eq. (52). From Table III we obtain $N_c \simeq 10 - 20$. With the usual molecular diameter of $\sigma \simeq 5.5 \text{ Å}$, this number projects into a length-scale of $\simeq 1.5 \text{ nm}$ for a spherical cluster or larger if relaxation is facilitated through chains of molecules. This length is in general accord with current estimates of spatial heterogeneities in supercooled liquids. The activation barrier scales quadratically with the number of units in the hot region compared to the linear scaling with the size of the cooperatively rearranging region of the Adam-Gibbs theory. However, there is no divergent length-scale in the present formulation.

Activated dynamics considered here do not anticipate the divergence of the relaxation time at any finite temperature, and the divergent solution given by Eqs. (61) and (63) is an artifact of the approximate integration used in Eq. (59). However, the empirically documented accord between $T_0$ and $T''$ is taken from Table III.
\[ C_p^\infty \simeq C_p^\infty \]
\[ T' = \frac{T_0^2}{T_g C_p(T_g)} \frac{\lambda}{\varphi_0^2} \]  
(65)

The temperature \( T' \) calculated from Eq. (65), with the thermodynamic parameters from Table III, is indeed close to the direct fit of Eq. (61) to experimental relaxation data (Table III). The parameter \( T' \) can also be related to the steepness fragility index [Eq. (63)]. Assuming \( T^{-1} \) scaling for \( C_p^\infty(T) \) in Eq. (61), one gets
\[ T' = \frac{T_g}{C_p(T_g)} \frac{m - m_{\min}}{m + m_{\min}} \]  
(66)

where \( m_{\min} = \log(\tau(T_g)/\tau_0) \simeq 16 \). Estimates of \( T' \) based on this equation are also listed in Table III. Since, for fragile liquids, \( T' \) is related to observable quantities through Eq. (65), one can derive the following relation for the kinetic fragility
\[ \frac{m}{m_{\min}} = 1 + \frac{(T_0/T_g)^2}{1 - (T_0/T_g)^2} \]  
(67)

This equation, which was previously derived by Ruocco et al., holds reasonably well for fragile liquids \( (m > 53) \). It makes a connection between the steepness index and the ratio \( T_0/T_g \) recommended by some authors as a measure of fragility.

Since the configurational heat capacity of fragile liquids is linearly related to the configurational entropy, \( s_c = s_0^c - C_p^\infty(T) \), Eq. (61) can be re-written in terms of the configurational entropy
\[ \ln(\tau/\tau_0) = \frac{D T'}{T + T'(s_0 - zs_0^c)} \]  
(68)

The current formulation still provides a link between the relaxation time and configurational entropy, but the algebra is different from the Adam-Gibbs relation [Eq. (6)]. The validity of either functional dependence of the relaxation time is often tested by calculating the slope of the glass transition temperature with pressure. Equation (61) suggests that \( T/T' - C_p^\infty(T) \) remains constant at the glass transition temperatures measured at different pressures. Following Goldstein, the condition \( d(T/T' - C_p^\infty(T)) = 0 \) provides the slope of the glass transition temperature with pressure, \( d_T/T' \). One needs to calculate the derivative of \( T' \) over pressure and the pressure and temperature derivatives of \( C_p^\infty \). The pressure derivative gives \( \partial C_p^\infty/\partial P_T = -T_g V_g \Delta \alpha_p^2/k_B \), where \( V_g \) is the molecular volume of the glass. The difference of the isobaric expansivities of the liquid and glass, \( \Delta \alpha_p \), is in the range \( 5 \times 10^{-4} \) K\(^{-1} \) (Refs. 44,118), allowing one to neglect the pressure derivative of \( C_p^\infty \). One then gets
\[ \frac{dT_g}{dP} = \frac{T_g}{T'} \frac{\partial T'}{\partial P} (1 - T'(\partial C_p^\infty/\partial P_T)^{-1} \].  
(69)

Equation (69) should be compared to what follows from the Adam-Gibbs scaling:
\[ dT_g/dP = T_g V_g \Delta \alpha_p/(S_c + C_p^\infty) \]  
(70)

Most data, available for strong/intermediate liquids, indicate that Eq. (70) adequately describes the experiment. Since \( \partial T_g/\partial P > 0 \) (Refs. 121,122,127), one can expect from Eq. (65) that \( \partial T'/\partial P > 0 \). The actual numbers for this derivative can be obtained from \( T, P \) relaxation data. The results of these calculations are given in Table III. The relaxation times were fitted to Eq. (61), at ambient pressure with \( D \) and \( T' \) considered as fitting parameters and experimental \( C_p^\infty(T) \) and ambient pressure. The parameter \( D \) was then kept constant at elevated pressures and \( \partial T'/\partial P \) was evaluated from the fit. The results of these calculations are in reasonable agreement with reported \( dT_g/dP \) and reproduce the drop of this derivative in going from fragile to intermediate glass-formers (Table III).

IV. DISCUSSION

The model developed here describes the thermodynamic properties of glass-formers in terms of statistics of excitations from a single-energy state of the ideal glass to a Gaussian manifold of configurationally unjammed states with higher energy and entropy. The model suggests that the thermodynamic signatures of fragile liquids, in particular a sharply increasing configurational heat capacity close to the glass transition, can be identified with the existence of a thermodynamic phase transition (“LL-line” in Fig. 14b), usually hidden below the glass transition temperature. The strong/fragile behavior is distinguished within the model by two parameters, the trapping energy parameter \( \lambda \) and the entropy gain for a single configurational excitation \( s_0 \), the ratio of
them equal to the experimental Kauzmann temperature \[\text{[Eq. (38)]}\]. Both parameters significantly decrease when going from fragile to intermediate/strong liquids, with the parameter \(\lambda\) showing the most significant change (Table [I]). Fragile liquids are therefore characterized by a broad range of configurationally excited states, whereas the energy distribution for intermediate/strong liquids is very narrow (Fig. [I]). Because of low values of either \(\lambda\) or \(s_0\) (or both of them) strong/intermediate liquids fall in the range of temperatures and excitation entropies \([T > T_c, s_0 < s_{0c}, \text{Eq. (31)}]\) not allowing a first-order transition.

The critical point \((T_c, s_{0c})\), separating fragile from non-fragile liquids (Fig. [I](a)), makes the descent into the energy landscape qualitatively different for them. The average basin energy of non-fragile liquids first starts to drop from the high-energy plateau according to the \(1/T\) law and then inflects into an exponential decay. The distribution of basin energies is narrow, and its maximum shifts to lower energies with cooling (Fig. [I](a),b). This behavior, often observed in simulations of binary LJ liquids, is well reproduced by the present model which places these fluids into the strong/intermediate category. As an example, we show in Fig. [I] the fit of the 1G model to Sastry’s data on binary LJ mixture (BLJM) \[28,131\]. The calculations were done for the highest density studied in simulations at which the BLJM liquid is most fragile. Equations \([28, \text{and (31)}]\) were used, respectively, for the configurational entropy and heat capacity, while Eq. \([61]\) was applied to the simulated diffusion coefficient. The excitation energy \((\epsilon_0 = 219 \text{ K})\) and the trapping energy \((\lambda = 71 \text{ K})\) obtained from the fit produce the following critical parameters: \(T_c = 35.5 \text{ K}\) and \(s_{0c} = 4.2\) (accidentally, \(T_c\) is close to \(T_K^{\infty}\)). On the other hand, the excitation entropy from the fit, \(s_0' = 0.32\), and the temperature range \(T > T_c\) together put the BLJM liquid into the category of intermediate fragility. With such low excitation entropy, the population of the excited state is close to 0.5 at high temperatures. From Eq. \([28]\) one then gets \((z = 1)\): \(S_0 = s_0'/2 + \ln(2) \approx 0.85\). The same number, 0.85, is reported by Sastry for the top of the enumeration function \(s_{c \max}^{\infty}\).

The behavior of fragile liquids is quite different. The configurationally excited state is almost entirely populated \((z \approx 1)\) in the entire range of experimentally accessible temperatures down to the glass transition. The average basin energy is almost temperature-independent, and the only effect of lowering the temperature on the distribution of basin energies is its narrowing according to the fluctuation-dissipation theorem (Fig. [I](c)). The invariant population of the configurationally excited states is abruptly terminated at the equilibrium first-order transition or (on supercooling) at spinodal instability at which point it drops to a low value representative of an entropy-poor, low-temperature phase as experimentally confirmed for TPP \[123\].

The fit of the model to experimental excess heat capacities and entropies of molecular glass-formers (Table [II]) has pushed the liquid-liquid phase transition below the glass transition. For some substances \([3,129,134,138]\) the thermodynamic liquid-liquid transition can be found above the glass transition. As an example of this situation, the 1G model is applied to excess entropy and heat capacity of laboratory water \[133,135\]. The thick lines in Fig. [I](a,b) show the results of measurements on bulk samples \([133]\) while open circles refer to samples confined in
3 nm pores of silica gel. The two sets of data coincide at high temperatures. Because of the limited temperature range of the bulk water data the fit to the thermodynamic 1G model is done for nanoconfined water (Table IV). The 1G model predicts a weak first-order phase transition at \( T_{LL} = 229 \text{ K} \) (\( P = 1 \text{ atm} \)). This number is very close to previous estimates for the temperature of crossing the “Widom line” at which the heat capacity gets a maximum and more recent measurements placing this point at 223 K. After the kink at \( T_{LL} \), the entropy slowly decays to zero at \( T_K \rightarrow 0 \).

The behavior of excess thermodynamic parameters of the laboratory water is compared to configurational parameters of SPC/E water obtained from constant-volume simulations of Starr et al. The fit of Eqs. (28)–(29) to the configurational entropy of SPC/E water (Fig. 17b) and Table IV yields a low excitation entropy \( s_0 = 1.3 \) below the critical value of \( s_{0c} = 4.0 \) [Eq. (37)]. The heat capacity curve then shows a broad pre-critical peak reminiscent of, but broader than, the heat capacity of nanofluid water (Fig. 17a). As in the case of the BLJM liquid, the excited state population, characterizing the configurational manifold, is slightly above 0.5 at high temperatures resulting in the plateau of the configurational entropy at \( z = 3 \) \( S_0 \simeq z(s_0/2 + \ln(2)) \simeq 4 \). This number is close to the estimate for the top of the enumeration function given by Sciortino et al. \( S_0 \simeq 3.7 \) at \( P \simeq 0 \).

The comparison of fits to laboratory and simulation data shows that the configurational part of the excitation entropy \( s_0 \) makes about 46% of \( s_0 \) for SPC/E water and only about 30% for \( o \)-terphenyl (Fig. 9). These comparable fractions of configurational components suggest that it is the change in the vibrational density of states (around the boson peak at \( \simeq 30 \text{ cm}^{-1} \)) caused by configurational excitations that is primarily responsible for the fragile behavior of glass-formers.

The configurational entropy from simulations can next be used to fit the relaxation times by applying Eq. (61). This procedure is straightforward for the Debye relaxation time and diffusivity obtained from constant-volume simulations at the same conditions as the data shown in Fig. 17a (see Table IV for the fitting parameters). The application to laboratory data is less obvious because of possible differences between configurational heat capacities at constant volume and constant pressure. Nevertheless, diffusivity of laboratory water can be fitted to Eq. (61), although with the fitting parameters (Table IV) requiring more fragile behavior (cf. triangles to open circles in Fig. 17).

Equation (61) is the central result of our modeling of

### Table IV: Fit of the 1G model to excess thermodynamics and diffusivity of laboratory water and to configurational entropy, diffusivity, and Debye relaxation time of SPC/E water from constant-volume simulations (\( \rho = 1.0 \text{ g/cm}^3 \)). The heat capacity and excess entropy of nanofluid water are used for the thermodynamic fitting. The energy parameters are in K, \( D \) and \( z \) are dimensionless.

| Liquid                  | \( \epsilon_0 \) | \( \lambda \) | \( s_0 \) | \( s_{0c} \) | \( z \) | \( D \) | \( T' \) | \( \log(\tau_0/s) \) |
|-------------------------|------------------|--------------|----------|-------------|------|-------|---------|-------------------|
| Bulk/Confined water     | 1298             | 649          | 2.8      | 2.0         | 3.0  | 66    | 19      |                   |
| SPC/E water             | 751              | 251          | 1.3      | 4.0         | 3.0  | 282   | 5.7     | -13.4             |
|                         |                  |              |          |             |      |       | 193     | 7.6               |

\( ^{a} \)From fitting the diffusivity of laboratory water according to Price et al. 
\( ^{b} \)Configurational component \( s_0 \) of the excitation entropy. 
\( ^{c} \)From fitting the Debye relaxation time.
\( ^{d} \)From fitting the diffusivity.
relaxation. It is also consistent with the empirically documented accord between the VFT and Kauzmann temperatures (Fig. 13). The model combines the thermodynamics of configurational excitations with the notion that assembling excited units in clusters is required for activated relaxation.\(^1\) The thermodynamics of glass-formers is thus determined by the statistics of excitations, while dynamics probe more rare events of clustering of excitations. One of the signatures of thermodynamic driving force behind relaxation is the realization of a dynamic fragile-to-strong transition close to the point where the heat capacity in the denominator of Eq. (61) reaches its maximum, \(C_P^{\text{max}}\). This sub-critical maximum is indeed predicted by the thermodynamic 1G model is the vicinity of the critical point \((T_c, s_{oc})\) (Fig. 14b). When the cooling path goes close to the critical point, the fragile non-Arrhenius dynamics changes to strong Arrhenius dynamics after passing the line of the heat capacity maximum ("Widom line"\(^2\) Fig. 13). A similar behavior has recently been observed for nanoconfined water.\(^3\)\(^4\)\(^5\)

Experimental evidence supports a link between the viscosity and configurational thermodynamics\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\) but this does not necessarily mean that activated events are driven by the entropy. Equation (61) still connects the relaxation time to configurational entropy [see Eq. (65)], but is based on standard arguments of activated kinetics in terms of excess kinetic energy accumulated at a "mobile unit". The model thus puts focus on the kinetic energy and its fluctuations as the main driving force of liquid relaxation.\(^12\) This notion brings relaxation of supercooled liquid in general accord with approaches developed to describe activated events in chemistry where accumulation of sufficient kinetic energy along a reaction coordinate, and not the entropy, is viewed as the general mechanism behind activated transitions. Since relaxation is understood in terms of clusters of excitations, the model can potentially bridge to more macroscopic arguments of elastic theories considering a region of shear displacements shoving the environment from a relaxing unit.\(^13\)

The present model does not anticipate a divergent length-scale and also avoids the need to consider the mosaic interface energies of Ref. \(^24\) which recent simulations have failed to support.\(^14\) It remains to be seen whether the formalism of configurational excitations\(^5\)\(^3\)\(^4\)\(^6\)\(^7\)\(^11\) "dressed" with the relevant excitance thermodynamics, provides a sufficient basis for the theoretical modeling of supercooled liquids. While the model yields a set of simple equations for some basic properties commonly reported for glass-formers [e.g., Eqs. (62), (68), and (61)], it should be recognized that the mean-field character of the model may push it too much into a strong first-order type of thermodynamic transition. Some "softening" of the model including fluctuations around the mean field would result in greater flexibility, but this would only come at the expense of an increase in the number of parameters.

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