Barrier Softening near the onset of Non-Activated Transport in Supercooled Liquids: Implications for Establishing Detailed Connection between Thermodynamic and Kinetic Anomalies in Supercooled Liquids.

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Abstract

According to the Random First Order Transition (RFOT) theory of glasses, the barriers for activated dynamics in supercooled liquids vanish as the temperature of a viscous liquid approaches the dynamical transition temperature from below. This occurs due to a decrease of the surface tension between local meta-stable molecular arrangements much like at a spinodal. The dynamical transition thus represents a crossover from the low $T$ activated behavior to a collisional transport regime at high $T$. This barrier softening explains the deviation of the relaxation times, as a function of temperature, from the simple log $\tau \propto 1/s_c$ dependence at the high viscosity to a mode-mode coupling dominated result at lower viscosity. By calculating the barrier softening effects, the RFOT theory provides a unified microscopic way to interpret structural relaxation data for many distinct classes of structural glass formers over the measured temperature range. The theory also provides an unambiguous procedure to determine the size of dynamically cooperative regions in the presence of barrier renormalization effects using the experimental temperature dependence of the relaxation times and the configurational entropy data. We use the RFOT theory framework to discuss data for tri-naphthyl benzene, salol, propanol and silica as representative systems.

A unified picture of the dynamics of supercooled liquids has emerged based on a theory of random first order transitions [1, 2, 3]. The mean field approaches to structural glasses exhibit two transi-
tions - one, an equilibrium transition at low temperature \(T_K\) corresponding to an entropy crisis of the type heralded by Kauzmann decades ago \[16\] and a high temperature transition, which is purely dynamic, at a temperature we call \(T_A\) \[1\]. The pure dynamic transition would be sharp for systems with infinite range interactions but for real liquids with finite range interactions it is actually a crossover that signals a change of transport mechanism from gas-like collisional dynamics to activated dynamics on an energy landscape. The dynamical transition is predicted generically via mode-mode coupling theories. Random first order transition theory analyzes motions in the energy landscape dominated regime by going beyond mean field to treat entropic droplets \[2\]. The creation of these droplets resembles nucleation at an ordinary first order transition but instead of leading to decay of a macroscopic metastable state droplet creation yields a mosaic of long-lived local structures in the liquid.

For a long time the cooperative regions predicted by this theory remained unobserved. During the last decade, however, a variety of experiments using nonlinear spectroscopies \[4\], single molecule techniques and scanning microscopies \[5, 11\] have revealed the dynamic heterogeneities that are intrinsic to this mosaic picture of the deeply supercooled liquid. Still more recently microscopic calculations based on the RFOT have made quantitative predictions both of the mean barriers \[3\] and the fluctuations of the barrier from region to region that give rise to nonexponential decay of measured time correlations \[9\]. These calculations give results that agree reasonably with experiment, using no adjustable parameters, thus providing a great deal of confidence in the underlying theory. The recent quantitative calculations expand around the low temperature entropy crisis transition that is extrapolated to occur at a temperature below those we can access without falling out of equilibrium. The purpose of this paper is to examine some of the corrections to the theory that arise from proximity to the high temperature dynamic transition at \(T_A\).

Near to the entropy crisis transition, the RFOT theory predicts that viscosity and structural relaxation times grow in a super-Arrhenius manner that can be described by the Vogel-Tamann-Fulcher (VTF) equation. We have argued before that deviations from this law are to be expected as one approaches the (mean field) dynamical transition temperature from below \[3\]. This is because the dynamical transition temperature, as viewed from the amorphous solid side, is a spinodal where there is a breakdown of the identity of the long-lived mesoscale structures of the mosaic. As we shall see the mosaic actually loses its identity at a somewhat lower temperature than mean field theory would predict.

In RFOT theory the approach to the spinodal from below leads to a softening of the interfaces of the mosaic, so the droplets shrink faster than expected as the temperature grows and the activation barriers fall faster. Equivalently said, the barriers initially grow faster upon cooling below the dynamic transition temperature than the VTF law determined by \(T_K\) would predict. The mode-
softening effects near a spinodal thus provide a natural explanation for the so-called high and low
temperature VTF fits that are sometimes used empirically for the viscosity and relaxation times.

The observed deviations from strict VTF behavior have previously been taken as evidence against
the idea that configurational entropy drives glassy dynamics in the activated regime. Here we see
the converse is true - the observed deviations are evidence that entropic droplets are the main
mechanism of glassy motions and that RFOT theory describes these excitations much better then
the older Adam-Gibbs argument \[6\], which makes no prediction of such mode softening effects.
We will show that by merely adding one material dependent parameter \(T_A\), the temperature of
the transition to landscape dominated behavior, the predicted barriers fit the data quite well.
In addition the remaining parameters have the dependence on measured configurational entropy
predicted by microscopic calculations. While the comparison of theory with experiment makes
the mode softening quite evident, the calculations we present are not a complete theory of the
dynamical crossover region - the mode coupling slow down predicted above \(T_A\) doubtless occurs
and will be reflected in specific aspects of the form of time correlation function decays. The pure
mode coupling results will be cutoff by droplet effects too before a strict divergence occurs. Thus
the temperature at which landscape effects start should not be taken as too precise. In addition,
near \(T_A\) droplets become so cheap in free energy terms that they may directly contribute to the
configurational entropy \[7\] which consequently becomes ambiguous close to \(T_A\). The ambiguity
of \(s_c\) has been explored before both from a strictly theoretical viewpoint \[2, 7\] and in the more
practical context of how to use calorimetric data properly to infer transport properties \[45, 43\].

The objectives of this paper are twofold. First of all, we demonstrate, by an approximate but
quantitative argument and by comparing with experiment that there is indeed droplet-droplet
interface softening due to order parameter fluctuations near the onset of activated transport, i.e.
at temperatures when the liquid is only marginally supercooled. We thus explicitly calculate
the structural relaxation barrier height in the entire temperature range where such a barrier has
a meaning. Further, and more ambitiously, we outline a framework of quantitative analysis in
which the details of the kinetic slow-down can be interpreted in all glassy materials. The explicit
calculations of the relaxation barriers given here allow one to clearly distinguish between the low \(T\)
regime where the activated methodology must be applied, and higher temperatures where mode-
coupling effects dominate, in spite of the presence of some activated processes. The temperature
of the crossover between the two behaviors is automatically deduced. We argue lastly that the
mode-coupling phenomena are strongly affected by the entropic droplets. It is not a goal of this
paper to provide for a convenient fitting formula, but instead we describe a particular fitting
procedure, directly tied to quantitative theory, to clearly discern the two distinct transport regimes
in supercooled melts. Nevertheless, we do end up discussing fitting issues in some detail, which has
made this article long if not at times tedious. One unavoidably develops a sense of appreciation of the problems faced by those who pioneered the already existing attempts at analyzing relaxation data without using a particular theory as a basis, in spite of much apparent variation in qualitative behavior among different chemical systems. In particular, we have come to the conclusion that any global fit to the kinetic data that fails to take account of thermodynamic data is dangerous because of the correlation of fitting parameters.

The organization of this paper is as follows: in the next section we review the entropic droplet picture, its microscopic implementation using density functional theory and describe how the theory quantitatively explains the phenomenology of both "fragile" and "strong" liquids. We then explore the mode softening expected near \( T_A \) presenting arguments using both scaling and variational ideas to quantify precisely how the mode softening changes the mosaic structure and the barriers. Following this, the resulting expressions are used to fit viscosity and relaxation time data for several specific systems where parallel thermodynamic data are available to us, so the softening affects can be tested. We will learn in which temperature range activated rearrangements dominate molecular transport. Remarks of general relevance to fitting the temperature dependence of rates will be made, using the microscopic picture uncovered by the RFOT theory. Finally we comment briefly on how mode softening effects will show up in experiments directly probing dynamic heterogeneity where deviations from strict VTF behavior have worried investigators.

1 The Random First Order Transition theory at the onset of activated transport in supercooled liquids.

The Random First Order Transition (RFOT) theory of the structural glass transition [3, 2] has provided a microscopic understanding of molecular motions in supercooled liquids, which we briefly review in what follows. A supercooled melt is obtained upon rapidly cooling the substance below its melting point, so that to avoid crystallization - a transition into the lowest free energy state available at these temperatures. Tautologically, each portion of the supercooled liquid is not in its true equilibrium state, but remains in a disordered, metastable state. In yet other words, each molecule of the substance is caught in a trap. Hence, molecular motions in such a supercooled system consist of groups of molecules switching between different traps: the current metastable structure containing the molecule must be destroyed while a new one created around the molecule’s locale. Alternatively said, molecular motions imply that locally, one solution corresponding to a minimum of the free energy functional (FEF) must be replaced by another. In order to quantify these notions one should compute the spatial extent of these local traps and the energetics of how one trap replaces another locally, as well as the mechanism by which such replacement occurs. This
is what the RFOT theory does. Consider as an empirical fact, that a compact region encompassing $N$ independently moving molecular units has $e^{s_e N}$ ways to pack itself comfortably into a metastable configuration at temperature $T$, where $s_e$ is the so called configurational entropy, per independently moving molecular unit (crudely speaking, this entropy is experimentally well estimated by the excess of the entropy of the supercooled liquid over that of the corresponding crystal, although differences of vibrational properties may alter this relation quantitatively). In our earlier language, $e^{s_e N}$ is the number of the free energy functional solutions in a region containing $N$ moving units, or, more concisely, “beads”. Determining the number of beads per molecule is an important issue in testing the theory essentially involving the issue of how to map the thermodynamics of a molecular fluid onto that of a nearly equivalent fluid of spherical entities. This will be discussed in great detail in the final section). A region of space that can be identified by a single mean field solution is called a mosaic cell. Trivially, the free energy of system of size $N$ that could freely switch between any two minima, is $-T s_e N$. However, in order to replace one solution by another, a nucleus of this new solution must be created within the old solution and this resulting entropic droplet would need to grow to replace the current molecular arrangement locally. Creating an interface separating two low free energy solutions must cost free energy, otherwise this new configuration would be a solution on its own, contradicting the original premise of having two distinct solutions in one region. The system with a domain wall, representing the growing droplet, may well resemble an external solution of the free energy functional but at a higher energy or effective temperature than the ambient system.

It turns out [2, 3] that this surface energy scales not with the surface area of the droplet, but in a more complicated way, so that the effective surface tension coefficient decreases for larger droplets according to $\propto 1/\sqrt{r}$, where $r$ is the radius of a (spherical) droplet. This unusual scaling is result of there being a multiplicity of distinct metastable molecular configurations in a supercooled liquid. The interface between two given (and generally à priori poorly matching) solutions can always be wetted by other, better matching, solutions. Such wetting does not occur for example at the solid-liquid interface in a regular crystallization transition, because the crystalline molecular arrangement is equally structurally different from any liquid packing, and therefore results in a large mismatch energy upon contact between those two phases. In the case of a supercooled liquid, in contrast, there is a near continuity of structures with a broadly varying degree of mutual disagreement, thus always allowing to find solutions mediating the costly narrow interface between two arbitrary minima of the free energy functional. The wetting argument was first conceived by Villain in the context of the random field Ising model (RFIM) [8], where the smooth landscape of the ferromagnetic spin-spin coupling is frustrated by a random static field. Even though all compromises are energetically inferior to the zero field translationally invariant Ising free energy, there are lots of them! (The analogy of the RFIM with structural liquids fails in one respect in that the RFIM model does not have the translationally invariant analog of the low energy crystalline arrangement that many
glass forming liquids could assume if cooled down slowly enough). In the RFIM, the surface tension renormalization due to wetting was estimated by calculating an energy gain of using a thicker interfacial region, made up by those wetting, less mutually frustrated solutions, at the expense of increasing the total area of the otherwise thin bare interfaces between two arbitrary solutions. This argument can be repeated, almost verbatim, for supercooled liquids [2], as long as the bare (unwetted) interface between two arbitrary solutions can be regarded as thin (i.e. comparable to the molecular length $a$). We will see shortly that this amounts to neglecting, in a mean field fashion, order parameter fluctuations at the temperature $T_A$ at which the longlasting metastable arrangements in the liquid start to persist. (This temperature also arises as a viscosity catastrophe in the mode-mode coupling theory [27, 28, 29]). Obviously, neglecting order parameter magnitude fluctuations is a good approximation away from $T_A$, and this assumption has lead to quantitative successes that we now list: First, the RFOT is the only microscopic theory that derives the barriers for structural $\alpha$-relaxation in supercooled liquids [3], using only the value of the heat capacity jump at $T_g$ as the input. The theory also has explained non-exponentiality of the $\alpha$-relaxation [9] above $T_g$ and its dependence on the liquid’s fragility, with no additional assumptions. Furthermore, it is the only existing theory that computes the cooperative length scale of those structural rearrangements (5-6 molecular diameters at $T_g$), without using adjustable parameters and that agrees with values found in many experiments [11, 12]. Knowing the cooperative length allows one to predict deviations from the Stokes-Einstein relationship between liquid’s viscosity and the particle’s diffusion coefficient [10], as confirmed by several measurements [11, 12]. Finally, it turns out that this length scale also dictates the spatial density of low energy excitations in glasses, observed at cryogenic temperatures [13], as well as the frequency of the Boson Peak and the thermal conductivity plateau in amorphous solids at low temperatures [14]. Before continuing our story, we feel we should comment on the molecular nature of the droplet interface tension, which could have so far appeared as a rather abstract concept to the reader. On the contrary, this tension is not abstract but is quite real and arises from stresses quantifying stretching (or contraction) of the inter-molecular bonds that would ordinarily hold together a metastable molecular configuration near a potential energy minimum but now mean that locally the region is in the vicinity of a saddle point. Therefore we always use word “activated events” to describe structural rearrangements in the supercooled liquid in the usual, chemical sense. The presence of activated dynamics and anharmonic deformations is one of the essential features of the RFOT theory, which makes it distinct from theories including only the purely collisional effects (those we discuss later in some detail in connection with the mode-mode coupling theory).

The RFOT theory thus states that at temperatures sufficiently lower than $T_A$, the free energy due to the entropic droplet formation $-\frac{4\pi}{3}(r/a)^3Ts_c$ is opposed by the interface formation surface
energy $4\pi \sigma(r)r^2$ to yield the following droplet growth free energy profile:

$$F(r) = 4\pi \sigma_K(r)r^2 - \frac{4\pi}{3}(r/a)^3Ts_c,$$

(1)

where $\sigma_K(r) \equiv \sigma_0(a/r)^{1/2}$ is the radius dependent surface tension coefficient, as expressed through the surface tension coefficient at the molecular scale $a$ - bead size:

$$\sigma_0 = \frac{3}{4}(k_BT/a^2)\ln((a/d_L)^2/\pi \epsilon).$$

(2)

Here, $d_L \sim 0.1a$ (for all substances) is the so called Lindemann length [15] - the size of thermal vibrations of a molecule at the mechanical stability edge of a solid. This Lindemann length is a central concept in the RFOT theory and in this paper, therefore we will discuss it in some detail below (the origin of formula (2) will also be discussed then). The RFOT theory indeed makes many quantitative predictions, as briefly summarized above, but perhaps more importantly it helps single out the universal aspects of the glass transition physics in wildly different chemical systems that superficially appear to have in common little more than the rapidly growing relaxation times as the temperature is lowered. We demonstrate this by quoting some of the universal relationships found in [3], that help one to see the common molecular origin of the glass transition in different systems. Indeed, combining Eqs.(1) and (2) yields (see the schematic in Fig.1):

$$F^\ddagger/T = \frac{3\pi[3/4 \ln(a^2/d_L^2\pi \epsilon)]^2}{s_c/s_c} \simeq \frac{32}{s_c},$$

(3)

where $d_L/a \simeq 1/10$ is the (universal) Lindemann ratio. According to Eq.(3), the extrapolated vanishing of the configurational entropy (at some temperature $T_K > 0$), discovered long ago by Kauzmann [16] would lead to divergence of the relaxation barriers in a supercooled liquid at that very temperature! The configurational entropy data are not readily available for many substances,
but the heat capacity jump $\Delta c_p$ is easier to measure. If one approximates $s_c$ near $T_K$ in a linear fashion according to $s_c \simeq \Delta c_p(T - T_K)/T_K$, one obtains that the relaxation times should diverge according to the empirical Vogel-Tamann-Fulcher (VTF) law: $\tau = \tau_0 e^{DT_K/(T - T_K)}$ and automatically recovers a very simple relationship between the liquid’s fragility $D$ and heat capacity jump $\Delta c_p$ per independently movable unit: $D = 32./\Delta c_p$. Thus, the RFOT provides a constructive argument on the connection between the kinetic and thermodynamical anomalies near the glass transition. Note that in the simple relationship in Eq.(3) the only temperature dependence of the activation exponent comes from the $T$ dependence of the configurational entropy. This is a consequence of the fact that the droplet surface energy scales with the temperature itself, as shown in [3] by a stability argument as applied to the liquid’s FEF. The value of the proportionality coefficient derived in [3] (leading to the 32. factor above) must be correct within a factor of order unity, however by good fortune it turns out to work very well in real substances as is without any corrections for larger interface width, suggesting the unwetted interfaces of the mosaic cells are indeed thin. Now, one simple consequence of Eq.(3), is that the magnitude of the configurational entropy per moving unit at the glass transition is theoretically predicted to depend only on the magnitude the relaxation time scale in the liquid:

$$s_c = \frac{32.}{\ln\left(\tau/\tau_0\right)}.$$  

On the other hand the glass transition temperature itself is defined as the temperature at which the generic (equilibrium value!) relaxation time in the system reaches a particular (large) value: $\tau(T_g) = \tau_0 \exp(F^\dagger/T_g)$. Therefore, the value of $s_c$ (per bead) at $T_g$ depends only on the glass preparation time scale, but not on the chemical nature of the substance! For example, if one patiently cools the liquid in a way that it is able to equilibrate on one hour scale: $\tau/\tau_0 = 10^5 \text{ sec}/10^{-12} \text{ sec}$, the resultant entropy is $s_c(T_g, 10^5 \text{ sec}) = 32./\ln(10^{17}) = 0.82$. Another common glass transition time scale - 100 seconds - would yield $s_c(T_g, 100 \text{ sec}) = 32./\ln(10^{17}) = 1.0$ Studying available thermodynamical data indeed shows all substances exhibit residual entropy of this magnitude at the glass transition (we will discuss how to determine the number of moving units per molecule in some detail later). We find it remarkable that a theory that uses no assumptions other than the existence of the glass transition itself (and uses no adjustable constants) should be able to provide the magnitude of this residual entropy and explain why its value should be so consistent among very different substances. No other theory has so far provided a microscopic basis for this consistency.

This is perhaps a good point to make some comments about what the essential assumptions in the RFOT droplet argument really are. Other than the surface tension $\sigma_0$ and the wetting effects that decrease it, many of its ingredients are well established on empirical grounds alone. The $s_c$ measured by calorimetry can and should be used in implementing the theory. The Lindemann parameter (that goes into determining $\sigma_0$) can be measured directly by neutrons. It is thus possible
to remain quite agnostic about the ultimate vanishing of \(s_c\) at \(T_K\) in applying RFOT theory to measurements. For the purpose of the RFOT theory, \(T_K\) is merely a convenient place to estimate \(\sigma_0\) because the free energy of a frozen minimum is then decomposable into a localization part and an interaction (see \[3\]), since the configurational entropy would vanish at \(T_K\). But if the comparison had to be made at the higher \(T_g\), \(\sigma_0\) would be smaller. This diminution is essentially related to the barrier softening dealt with in this paper. The \(r\)-dependence of the surface tension from the wetting requires a sufficient multiplicity of states and nothing more. Again, a precise \(T_K\) (referring to a strict non-analyticity rather than a cross-over) is not needed to have this effect. If a multiplicity of states exists, in any event, there will be a strong reduction of the surface term from a naive surface energy as the displaced region grows in size. Deviations from the \(1/r^{1/2}\) behavior can be at most a factor of two in the size range that can be explored to date in liquids without involving supercosmological waiting times. If indeed there is no crisp \(T_K\) but rather a smooth turnover to an \(s_c\) that strictly vanishes only at absolute zero nothing about the predictions would be changed in the temperature range that can be currently measured.

We point out to those scientists who, as a matter of faith, prefer a smooth turnover in entropy rather than a sharp transition at an entropy crisis that a complete theory in those terms requires in our view a specification of what the \(T = 0\) state actually is supposed to be and also how one should compute the excitation energies from it. The only concerted attempt in that direction that we are aware of is Nelson’s theory [18] which, roughly speaking, suggests a Frank-Kasper phase as the ground state and disclinations as the defects. Calculating the dynamics of disclinations at their relatively high density above \(T_g\) however remains still open in that theoretical picture: the mere existence of such defects would in no way be in direct contradiction to the present arguments. Nussinov [19] has recently argued that the icosahedratic Hamiltonian has a uniformly frustrated glass transition much like that predicted for stripe phases [20] and therefore would be described by RFOT theory, in so far as its dynamical behavior below \(T_A\).

Another basic prediction of the RFOT theory has to do with the length scales pertinent to the motional degrees of freedom in the activated transport regime. First of all, the critical radius for droplet nucleation is, as easily shown from Eqs. (1)-(3),

\[
r^\perp/a = (3\sigma_0 a^2 / 2T s_c)^{2/3} \simeq \frac{2.0}{s_c^{2/3}}, \tag{5}
\]

where \(s_c\) is per moving unit. Hence, like the configurational entropy, the critical radius depends only on the cooling rate at the moment the liquid falls out of equilibrium. For example, at \(\tau\)’s on an hour scale, \(r^\perp/a \simeq 2.3\). This correspond to reconfiguring about 48 beads - a rather large (but mesoscopic) number. While the volume of the critical transition state droplet dictates the smallest number of molecules that needs to be summoned up in order to convert a given region from one structural state to another, the volume of the liquid that must ultimately reconfigure to a state of a
similar energy density is found from a slightly different requirement. Indeed, the free energy profile for droplet rearrangement from Eq. (11), though very similar to a regular nucleation theory, is quite distinct in the sense that the state on the other side of the barrier is not a different phase of the substance, but is really another liquid state! To give an analogy, alternative liquid (or, amorphous) packings are different in specific structural detail yet are generically the same, just like fingerprints of different individuals. Therefore at the droplet size $r^*$ determined from $F(r^*) = 0$, the liquid is guaranteed to be able to arrive to any liquid state typical of this temperature. Thus to achieve an irreversible arbitrary translation of an individual molecule will require rearrangement of fluid within radius $r^*$. If a smaller amount than $4\pi/3(r^*/a)^3$ is reorganized, the resultant local energy density will be higher and the region is likely to revert for its original configuration. On the other hand, if a region of radius $r^\dagger$ is rearranged, that rearrangement will continue to expand until it extends a distance $r^*$, roughly. Eq. (11) strictly would imply spherical droplet geometry but fluctuations from such shape are likely because of the fractal wetting of the mosaic cell interface [8]. At any rate, we would like deduce a volume density of the cooperatively rearranging molecular structures; to this end we prefer to use a volumetric length scale $\xi$, defined as $(\xi/a)^3 \equiv (4\pi/3)(r^*/a)^3$. Consequently,

$$\frac{\xi}{a} \simeq \frac{5.1}{s_c^{2/3}}. \quad (6)$$

At the one hour scale glass transition $\xi$ is about 5.8 moving units. Cooperative lengths of this size have been observed in experiments, as already mentioned. The number of those units in a cooperative volume $(\xi/a)^3$ is about 200, but will be smaller at higher temperatures, as is easily seen using Eq. (6) when we remember that $s_c$ grows with temperature. To summarize the idea of cooperativity, in order for even a single molecule to perform a translation, a large number of molecules must be moved as well, otherwise the particle is likely to return to its original location. The magnitude of each individual molecular translation is about the Lindemann length $d_L$. Such cooperative rearrangements are intrinsic degrees of freedom in glasses that exist due to the non-equilibrium nature of the glass transition. Their quantum counterpart is the origin of the two level systems in glasses seen at cryogenic temperatures [13]. The whole sample at any instant of time may be imagined as a mosaic of individually cooperative domains of roughly the size $\xi$ [3].

Again, according to the RFOT theory, the values of $s_c$ and $\xi/a$ at the glass transition mostly depend on the most probable relaxation rate in the substance, but not much on chemical detail. While it has been known for a while that the configurational entropy per molecular unit is about the same for all substances at $T_g$, explicit measurements of the cooperative length have been carried out only relatively recently, but they do recover a length of the order several molecular spacings. Clearly, without a constructive argument for the mechanism of the relaxation and the corresponding barrier height, the existence of these universalities would thus be rather mysterious. While here we see these universal patterns are quite natural, in contrast the venerable Adam-Gibbs (AG) approach
does little to justify the correctly estimated $F^\dagger \propto 1/s_c$ dependence, whose validity near $T_K$ we can now finally understand. Indeed, the AG argument is not rigorously speaking a kinetics based theory; instead in the AG paper, the estimates of the probability to overturn a region was based on a detailed balance requirement, something that specifies only *relative* rates.

Finally we note that the universal relationships from Eqs. (4)-(6) will be somewhat modified when the interface softening effects are taken into account. The non-universal corrections will be especially pronounced in the proximity of $T_A$, where the barriers for structural rearrangements vanish. Conversely, substances with a smaller ratio of $T_A$ to $T_K$ will exhibit larger deviations from universality at the laboratory glass transition temperatures.

### 1.1 Onset of non-activated dynamics at $T_A$: A temperature driven Spinodal Transition between alternative metastable molecular packings.

From the liquid state viewpoint it makes sense to take a closer look at what happens in the liquid when it is cooled below $T_A$, where the barrier for structural rearrangements in liquids begins to appear. We know of two different, but related ways to formally analyze phenomena at $T_A$. One is the so called Mode-Mode coupling theory (MCT) \cite{27, 28, 29}, the other is the Density Functional theory (DFT) \cite{30} or the nearly equivalent self-consistent phonon argument \cite{31}. A dynamical transition at a temperature $T_A$, at which the liquid’s viscosity diverges, was discovered by using the MCT. Although the result of an elaborate self-consistent computation of the liquid’s particle auto-correlation function, this transition can be pictures microscopically as a crowding phenomenon of a sort: molecules get in the way of each other’s motion, and at a certain temperature their thermal motion is so slow that they cannot get out of each other’s way and thus effectively arrest their mutual displacement. This dynamical arrest appeared also, in what at first seems a little related manner, in the DFT and the self-consistent phonon theory \cite{30, 31}. Those appear to be *static* theories, which show that at low enough temperatures, the molecules would give up their translational entropy in favor of localization and forming aperiodic lattices! What would be the form of the free energy functional that would let us detect such singularity and what is the order parameter that would serve as the argument of this functional? We shall see an effectively useful choice is quite simple. We reiterate that we are considering here a localization transition below which a molecule settles down with its surrounding in a metastable manner for times longer than the thermal equilibration times, or several molecular vibrations, or, equivalently at these temperatures, a few molecular mean passage times. Such a situation is not a theoretical speculation, but is the sensible meaning of neutron scattering experiments that show a long plateau in the time dependent structure factor \cite{21}. At a first glance, since the liquid (as empirically known from calorimetry) still has an enormous number of alternative low density aperiodic structures at temperatures where the plateau is seen, it seems one
must have just as many order parameters to describe completely all those alternative outcomes after
the transition takes place. This is directly related to the necessity of introducing replica symmetry
breaking (RSB) in mean field spins glass models [17]). Yet, again, while in detail each of these states
is different, they do have common statistical properties. Describing the RSB is complicated enough
in infinite dimensions, but here we need to work with its consequences in three dimensions. There
is a way to make quantitative progress, if one realizes that the problem can be divided into two
relatively separate parts. Assessing the free energy change due to the topological, or localization
part of the transition can be separated from the combinatorial component, which has to do with the
multiplicity of the alternative structures below $T_A$ corresponding to the same degree of packing. The
localization contribution was studied in [30] by calculating the free energy of a particular aperiodic
structure depending on the degree of localization as measured by the inverse of the length scale $\alpha$
characterizing the spread of the molecule’s coordinate probability distribution: $\rho(r) \equiv \rho(r, \{r_i\}) =
\sum_i (\frac{\alpha}{\pi})^{3/2} e^{-\alpha |r - r_i|^2}$. Clearly, $\alpha = 0$ describes a completely delocalized liquid state, while $\alpha \rightarrow \infty$
corresponds to freezing into an infinitely rigid lattice. Therefore, $\alpha$, if sufficiently large, can also be
interpreted as the spring constant of an Einstein oscillator restraining each molecule to its location
in the aperiodic lattice, hence the term self-consistent phonon theory. In [30], the density profile
$\rho(\{x_i\})$ was used as a variational anzatz in the Ramakrishnan and Yussouff [32] density functional:

$$F[\rho(r)] = \int d^3 r \rho(r)[\ln \rho(r) - 1] + \frac{1}{2} \int \int d^3 r d^3 r' [\rho(r) - \rho_0]c(r, r'; \rho_0)[\rho(r') - \rho_0] + F_{uni}. \tag{7}$$

Here, $F_{uni}$ is the excess free energy of the uniform liquid, and computing the interaction term
requires knowing the direct correlation function $c(r, r'; \rho_0)$. $\rho_0$ is the average density. Finally,
we repeat, the set $r_i$ correspond to the coordinates of the vertices of a particular amorphous
lattice. Given the $\rho(r)$ anzatz, $F(\alpha)$ can be computed numerically for any lattice (the details of the
calculation along with the a discussion of the accuracy of the approximations used can be found in
[30]). We note that other procedures have also lead to the generation of aperiodic free energy
minima on computers [22, 23]. The main result is that now we have a free energy as a function of a
single averaged scalar order parameter $\alpha$ that characterizes localization of the liquid’s molecules into
amorphous packings. While at low densities a uniform liquid situation $\alpha = 0$ is the only minimum
of $F(\alpha)$, at some high density/low temperature a secondary minimum appears at $\alpha$, signalling a
free energy non-analiticity. This is illustrated in Fig.2. The actual position $\alpha_0$ of this secondary
minimum depends on temperature; it is of the order 10 at $T_A$, but increases to become around $10^2$
closer to $T_g$. Still, what can the thermodynamical significance of this near spinodal minimum in so
far it is much higher in free energy than the delocalized state with $\alpha = 0$? This significance may
be hard to appreciate until one recalls that even though each aperiodic structure with $\alpha_0 \sim 10^2$ is
indeed only metastable energetically, there are exponentially many alternative aperiodic structures
as indeed reflected in the large value of configurational entropy. Furthermore, the value of the free
Figure 2: This is a schematic of the free energy density of an aperiodic lattice as a function of the effective Einstein oscillator force constant $\alpha$ ($\alpha$ is also an inverse square of the localization length used as input in the density functional of the liquid. Specifically, the shown curves characterize the system near the dynamical transition at $T_A$, when a secondary, metastable minimum in $f(\alpha)$ begins to appear as the temperature is lowered.

energy at the metastable minimum is exactly equal to $T s_c$ at the corresponding temperature! This has been rigorously shown for the Potts Glass, which also exhibits a dynamical arrest at $T_A$ \[1\] and has similar symmetry properties to the structural glasses. Recent explicit replica approaches of structural glasses also make this point clear \[33\].

According to the definition of $\rho(r)$, the inverse square root of $\alpha$ corresponds to the localization length scale of a molecule at $T_A$. Alternatively, this length scale must be equal to the amplitude of thermal vibrations of atoms around their metastable equilibrium positions at the edge of mechanical stability of a sample. The concept of this length scale was introduced long ago by Lindemann \[15\]. Empirically the Lindemann length $d_L$ is known to be about one tenth of the molecular size $a$ from the magnitude of the plateau measured in neutron scattering \[21\]. In addition to the DFT and self-consistent phonon studies, later calculations using more sophisticated, replica machinery \[33\] confirmed the appropriateness of $\alpha$ as the order parameter for the transition at $T_A$, as well as its numerical value at the transition. The density functional theory explains the appearance of the Lindemann ratio $d_L/a$ in the formula \[2\] for the molecular surface tension coefficient between different aperiodic structures. Though it was the result of a detailed calculation using the free energy functional from Eq.\[7\], formula \[2\] can be understood in simple terms by recalling the expression for the free energy of a monatomic gas per particle: $F_{\text{ideal}}/N = \frac{3}{2} \ln \left( \left( \frac{2\pi \hbar^2}{mT} \right)^{2/3} \frac{mT}{2\pi N} \right)$. The surface energy due to $\sigma_0$ is one half the free energy cost of the entropy loss of a particle forced to be within a (localization) length $d_L$ instead of the “legally” allowed length $a$, corresponding to the liquid’s volume per molecule $V/N = a^3$ and relevant to interchanging particles’ identities. Lastly, we can already observe that due to the fluctuations of the meanfield order parameter $\alpha$ at the spinodal temperature, a sharp molecular interface can not be realized. Moreover, due to the smallness of
the barriers at the spinodal, which we estimate in the next subsection, the surface tension between alternative molecular packings will nearly vanish thus resulting in very small droplets and extreme ease of their formation. This is what we call *interface softening*.

The bare surface tension from the density functional argument for a sharp interface between different aperiodic structures $\sigma_0 = (3/4) \log(100/\pi e)(T/a^2) \simeq 1.85(T/a^2)$ is actually quite close to the simulated surface tension of a hard sphere crystal approaching a hard wall [21]: $\sigma_{wall} \simeq 2.0T_m/a^2$. The surface tension between a periodic crystal and its melt is lower [25]: $\sigma_{XM} = 0.61T_m/a^2$ owing to the broadness of the crystal-melt interface. We notice however that the empirical validity of Turnbull’s rule [26] suggests that the crystal/melt value is indeed universal. This is entirely analogous to our assumption that $\sigma_0$ is universal and should vary little from substance to substance.

Returning to the very beginning of this subsection, one may note that it is not at first site obvious that the dynamical viscosity catastrophe predicted by MCT and the DFT’s localization transition at $T_A$ should describe the same real life phenomena. Nevertheless, this is indeed the case, as shown in [34]. That work exploited the fact that the density functional allows one to derive both the equilibrium value of the static order parameter $\alpha$, and the molecular auto-correlation function, whose long time asymptotics depends on $\alpha$ as well. Moreover, in the infinite dimensional limit the self-consistent equations determining the localization length are identical in both descriptions. We mention this yet for another reason. Even though we will use the static formalism to estimate the droplet surface tension close to $T_A$ and thus deduce the value of the corresponding nucleation barriers, the dynamical perspective supplied by the MCT will be necessary to achieve a full quantitative description of the viscous phenomena at the very onset of activated transport, where the crowding effects are primarily responsible for the kinetic slowing down. Conversely, we now understand that the kinetics of these droplet rearrangements is influenced by the smallness of the spinodal barriers in the vicinity of $T_A$, therefore the analysis of the interface softening should be done self-consistently.

There is another, very important point we must mention here. So far we have lead our discussion as in this paper if the transition at $T_A$ occured as a sharp point in real liquids. Actually, this transition is avoided due to appearance of activated transport, or the entropic droplet excitations, as noted long ago in [2]. According to the MCT itself, at some temperature ($T_A$) the liquid’s viscosity would become strictly infinite. Yet clearly molecular molecular motions that involve larger fluctuations than the Gaussian fluctuations presented in the MCT are possible but rather unlikely. These are the “activated events”. Hence, below MCT’s $T_A$, the activated transport must begin to dominate. In the context of liquid helium, Feynman once argued [36] that the very definition of something being a liquid means there can be no barriers. In fact there is no contradiction with his suggestion, because the barriers are between states that correspond to quenched aperiodic solids structurally nearly identical to the energy minima. A similar sentiment underlies Kuhn’s theorem of viscous
1.2 Estimate of the barriers close to $T_A$.

In this subsection we estimate the effects that interface softening near $T_A$ will have on the value of the droplet surface tension, assuming we know $T_A$ as an input parameter of the calculation. The approximate functional form we obtain will be then used to fit the experimental $T$ dependences of the log-relaxation time for several systems.

Estimating the surface tension between distinct phases can be done in several ways. If a free energy functional describing all of the phases of the system is known, there is a straightforward mean-field recipe allowing one to complete the task (see for example [35]), for a given droplet geometry, or order parameter values at the boundaries etc. This is done by integrating the free energy density, given by the functional, throughout the interface region. Qualitatively, this amounts to multiplying the functional’s barrier height per unit volume (it has the units of energy density!), computed using an appropriate reference, by the interface width. At a second order transition, for example, the latter is approximately equal to the (diverging) correlation length.

Such a calculation close to $T_A$ can be done, in principle, by using a computed functional $f(\alpha)$, allowing $\alpha$ to be a function of $r$. One sticking point is that realistic, dense fiducial structures characteristic of minimum free energy structure found near $T_K$, cannot be easily generated with current simulation algorithms in a reasonable time. One has to extrapolate to find their statistical properties. The earlier RFOT theory calculations circumvent this problem (in fact the closer to $T_K$, the better it should work) by using the (measured) Lindemann ratio and assuming a sharp interface. Near $T_A$, a more detailed free functional would apparently have to be used. Nevertheless, the surface tension near $T_A$ can be estimated via a scaling argument. Since both limits, at $T_K$ and $T_A$, are under some control, an interpolated formula for intermediate temperatures can be developed.

Let us address the surface energy term in the high temperature regime close to the spinodal at $T_A$. Let us first compute the surface tension at a regular spinodal transition occurring near a critical point. We must note, the issue of the interface energy between alternative amorphous packings, as described by $f(\alpha)$, is however different from a regular spinodal involving only two distinct phases, in the following way. To determine the surface tension between any of the amorphous structure and the delocalized uniform liquid state, one must compute the “contents” of the underbarrier region, as shown by the shaded area in Fig.3(a). The arrow above the shaded area denotes a “transition between” a localized and the uniform state. On the other hand, in order to calculate the solution-solution interface energy, one must remember that $f(\alpha)$ is not the full energy density, but only a projection of the full functional onto a one-dimensional surface, parametrized by $\alpha$. A
transition between two structurally unrelated states and back is shown by a double-ended arrow now in Fig. 3(b)). Clearly the barrier for such a transition can not exceed $\Delta f$ (from Fig. 3(b)), because one can always find a sequence of states of the liquid connecting two arbitrary metastable minima. The highest energy state is the top of the barrier because this point is accessible from any of the amorphous structures (and the uniform state, of course). The droplet-droplet barrier energy is shown the shaded region in Fig. 3(b). $\Delta f$ gives therefore the upper limit to the excess free energy density between two solutions required to connect two different minima characteristic of the temperature $T$. It, along with the width of strained region, is needed to estimate the bare surface tension overall.

Using a generic analytical expression for a functional $f(\alpha)$ exhibiting a spinodal transition at $T_A$, we can estimate $\Delta f$ close to $T_A$. A number of simple functional forms for $f(\alpha)$ can be used that involve only a few constants. We propose a form that has as many constants as we can fix using the known theoretical constraints. Consider the following free energy density:

$$f(\alpha) = T_A s_c^A \left[ 1 + (1 + c_1 t) \left( \frac{\alpha}{\alpha_0} - 1 \right)^3 - c_1 t \left( \frac{\alpha}{\alpha_0} - 1 \right) \right],$$

where $s_c^A$ is the configurational entropy at $T_A$, $t \equiv \frac{T - T_A}{T_A} > 0$ is the reduced temperature, and $c_1$ is some yet unknown (positive) constant. The functional in Eq. (8) already satisfies some constraints, known from [30]. First, it yields a spinodal transition at the value $\alpha = \alpha_0$ of the order parameter, when $T = T_A$. Secondly, $f(0) = 0$ - the liquid only has the uniform component. Now call $\alpha_0(T)$ the position of the metastable minimum of $f(\alpha)$ from Eq. (8) at any $T < T_A$ ($\alpha_0(T_A) = \alpha_0$, of
course). Note, while the functional in Eq.(8) does satisfy $F[\alpha_0(T_A)] = T_A s_c(T_A)$ automatically, it is too simple to reproduce the constraint $F[\alpha_0(T)] \leq T s_c(T)$ at an arbitrary temperature (for example, the height of the inflection point of this $f(\alpha)$ is temperature independent). Still, it has the expected physical feature of exhibiting the spinodal type scaling at $T_A$ (such as the one occurring in the Potts Glass at $T_A$). In view of what was just said, we only need a qualitative estimate for constant $c_1$. This is easily obtained by requiring, for example, that $F[\alpha_0(T_K)] = T_K s_c(T_K) = 0$. A simple calculation shows that $c_1 = 3/t_K$, where $t_K \equiv (T_A - T_K)/T_A$, and therefore

$$\frac{\Delta f}{T_A s_c^3} = 4 \left( \frac{t}{t_K} \right)^{3/2} \frac{1}{\sqrt{1 + 3(t/t_K)}}. \quad (9)$$

The argument leading to Eq.(9) is crude, but yields physically reasonable results. It gives the expected scaling of the barriers with temperature, and the absolute energy density scale is determined by $T_A s_c(T_A)$ - the only available parameter with these dimensions. The numerical coefficient is not very well determined but it does turn out to work well enough to make clear a main point of this paper, namely the existence of interface softening at $T_A$.

An elementary calculation that yields that the corresponding free energy curvature at the minimum at $\alpha_0(T)$ gives a scaling $t^{1/2}$, which leads to the correlation length scaling at the transition $\xi_A \propto t^{-1/4}$. These mean field scaling results for an ordinary spinodal transition were obtained, of course, long ago by Binder [38] for a magnetic field driven spinodal transition in an Ising spin system. Kirkpatrick and Wolynes identified this length scale as of interest near $T_A$ a long time ago [1]. This length scale $\xi_A$ is also the length scale associated with replica theoretic and mode-coupling theories of dynamical structural inhomogeneities in supercooled liquids [39]. Now, if it were not for the entropic droplet excitations below $T_A$, our estimates for the surface energy at $T_A$ would simply involve the excess free energy of a planar surface $\sigma_A \sim \Delta f \xi_A$. But at $T_A$ the barriers for structural relaxations vanish (remember $\sigma(T_A) \propto \Delta f$). Since infinitely small barriers imply infinitely small droplets, this means that the correlations on the diverging length scale $\xi_A$ simply cannot be established, because it costs no energy (and time) for the material to reconfigure at these temperatures. In other words, the interface of such a small droplet cannot be taken as a plane. However, a droplet cannot be smaller than the molecular size $a$. This length therefore is the appropriate length scale for the inhomogeneous saddle point solution close enough to $T_A$. A better estimate for the surface tension to compute the entropic droplet cost is, as a result, $\sigma_A \sim \Delta f a$. On the other hand, there should be little to no wetting in this regime. We repeat that this is because the order parameter fluctuations exclude the possibility of having a narrow droplet-droplet interface. Alternatively said, wetting cannot take place on length scales smaller than the $\xi_A$, that would be appropriate in the absence of the entropic droplets. Hence, the surface energy term close to $T_A$ should have a regular, quadratic, scaling with the droplet’s size (which in any event will prove to be quite small).
We thus establish that the following droplet surface energy terms are valid at the opposite ends of the temperature interval $T_K < T < T_A$. At $T_K$, $\Sigma_K = 4\pi \sigma_K(r)r^2 = 4\pi \sigma_0 a^2(r/a)^3/2$. At $T_A$, on the other hand, $\Sigma_A = 4\pi \sigma_A r^2 = 4\pi \Delta f a^3(r/a)^2$, where $\Delta f$ given by Eq.(9) should be an adequate approximation. Note, at low enough temperatures, the barrier estimate at $\Sigma_A$ will exceed the $\Sigma_K$ term (wetted or not). At high temperatures (closer to $T_A$), the cheapest way for the system to reconfigure is to jump over the low spinodal barriers (even though this process is somewhat modified by the entropic dropets destroying long range correlations at $T_A$). In this regime, the viscosity will in fact be determined not by the activated kinetics since the individual molecular configurations are short lived, but rather by the crowding effects of the mode coupling theory. However, as $T_K$ is approached, the mode coupling relaxation times would diverge, and the spinodal barrier becomes larger than that of the entropic droplet rearrangements (wetted or not, actually). The entropic droplet rearrangements become the main contributors to the molecular motions in the liquid. A simple interpolation formula, that allows the system to choose the smallest available barrier, is provided by the following expression for the droplet energy growth, for instance:

$$F(r) = \frac{\Sigma_K \Sigma_A}{\Sigma_K + \Sigma_A} - \frac{4\pi}{3} r^3 T s_c.$$ (10)

Obviously, the ratio in the r.h.s. of Eq.(10) tends to $\Sigma_K$, as $T \to T_K$, and vice versa, to $\Sigma_A$ around $T_A$. One should regard our argument as a variational calculation for what would otherwise be a complex replica instanton calculation. There is more than one way to make an interpolation of this kind. We feel this ambiguity, however, is unimportant for the following reason: We will be use the functional form of $F(r)$ in Eq.(10) to fit the experimental log $\tau$ vs. $T$ data in the following section, using $T_A$ as the fitting parameter. Even if this form of the surface term is not exactly correct, varying $T_A$ should be able to compensate for any inaccuracy to some extent. Similar reasoning applies to any degree of uncertainty about the exact functional form and value of the barrier at $T_A$ calculated earlier in this section. This can also be absorbed into the best fitting value of $T_A$, provided the functional form in Eq.(10) is flexible enough. We will see à posteriori that it is flexible enough indeed, at the temperatures where the liquids viscosity is due to the activated character of the molecular transport, not the MCT effects, that is at the values of viscosity around 10 poise and higher. What is the meaning of the value of $T_A$ that is obtained? $T_A$ provides an estimate of the temperature at which a soft crossover to the onset of activated transport takes place. Since this is not a sharp transition, it is perhaps inappropriate to worry about the inaccuracy of $T_A$. We may at least qualitatively compare ratios of $T_A$ to $T_K$ with detailed microscopic calculations. Our main goal here is to show that the phenomenon of interface softening is consistent with available experimental data. And it is indeed, as we discuss in the following section. Lastly, one should anticipate from Eq.(10) that substances with a smaller value of the $T_A/T_K$ ratio will exhibit more pronounced deviations from the simple $F^\ddagger \propto 1/s_c$ predicted neglecting the softening effects. It should be already obvious from the discussion leading to Eq.(10) not only that the surface tension
will disappear at $T_A$, but also the RFOT scaling of the barrier with inverse configurational entropy will be replaced by a conventional $F^\dagger \propto 1/s_c^2$ valid in the absence of wetting near $T_A$. Such a result was obtained by Kirkpatrick and Wolynes \cite{11} and is described as the result of replica instanton calculations for structural glasses by Parisi \cite{40} and by Takada and Wolynes for random heteropolymers \cite{41}.

2 Fitting and Interpreting Experimental Relaxation Times.

In this final section of the article we discuss the implications that mosaic interface softening has for the temperature dependences of the apparent relaxation times in supercooled liquids. The existing RFOT theory calculations provide a complete microscopic picture of activated transport in these systems, and a quantitative description of the kinetics sufficiently close to $T_K$. Furthermore we will show here that the RFOT theory can provide a constructive basis to analyze the log $\tau$ data for all compounds on the same footing through nearly the entire range of liquid state conditions. Heretofore such a universal analysis has usually been considered difficult for the following reasons:

On the one hand there is the obvious common feature of a dramatic kinetic slowing down in all glassy systems. Furthermore, it seems all known systems exhibit to some degree two types of kinetics commonly known as structural, slow $\alpha$-relaxation, that we focus on in this work, and faster $\beta$-processes. The slow $\alpha$-relaxation is normally straightforward to separate from the $\beta$ processes and it exhibits many similar features among different systems, most prominently a rapid growth, that is often fitted with the VTF form. Since the work of Adam-Gibbs \cite{6}, where $F^\dagger \propto 1/s_c$ was suggested, many purely empirical attempts have been made to establish a connection between the Kauzmann’s entropy crisis at $T_K$ and the relaxation time divergence. But these attempts are stymied because, unfortunately, the $\tau(T)$ dependences, while covering many orders of magnitude, show, one may even say, qualitative differences in how the grow with decreasing temperature when looked at very carefully. For example, stronger substances tend to appear almost Arrhenius-like, tempting an interpretation using a simple activated event as the transport mechanism; fragile substances (like salol or TNB) exhibit a pronounced turnover in log $\tau(T)$ that is not entirely satisfactorily fit by a single VTF law. Still, perhaps with an exception of polymeric melts \cite{50}, where detailed analyses pose some problems (to be discussed below), an unambiguous connection between the kinetics and thermodynamics of many glasses has been established in several recent works \cite{21, 43, 44}. It seems beyond reasonable doubt that the decrease in the configurational, or excess liquid entropy with temperature is, at the least, qualitatively correlated with the observed concurrent rapid growth of the relaxation times, as supported by analyzing many substances. As we have already mentioned, this correlation is predicted by the RFOT theory, which not only gives a constructive argument in
support of the relation $F^{\parallel} \propto 1/s_c$ conjectured by Adam and Gibbs early on but also computed the proportionality coefficient on a microscopic structural basis. Experimentally, this latter relationship was convincingly demonstrated to work well close to $T_g$ for several substances for which both thermodynamical and kinetic data are available \[45\]. As mentioned earlier, the RFOT theory predicts that close to $T_K$, when $s_c \simeq \Delta c_p(T - T_K)/T_K$, $F^{\parallel} \propto 1/(T - T_K)$ and the VTF should describe well the temperature dependence of the relaxation time magnitude.

While the VTF works globally well for many substances, some materials seem to require more complicated functional forms over the measured temperature range. In those systems, the low $T$ part of the data could still be fitted by the VTF, however the exact choice of which part of the experimental curve to use in the fit introduces a considerable degree of ambiguity. We know of several, unrelated attempts to deal with this ambiguity. One is to make a simultaneous plot of $1/F^{\parallel}$ versus $s_c(T)$ as elegantly done by Richert and Angell in \[45\] in the context of checking the AG relationship (we feel this is the most direct way to see a correlation between thermodynamics and kinetics in supercooled liquids, and find the evidence demonstrated in \[45\] compelling). Another approach is to plot $[d \log \tau/d(1/T)]^{-1/2}$ vs. $1/T$ \[51\] (a VTF functional form would appear as a straight line, when graphed in this manner). This way of presenting the data suggests, purely empirically, that at least three distinct regimes of relaxation are observed in substances such as salol or TNB (from the RFOT point of view, those regimes could correspond to the collision and activation dominated transport and an intermediate behavior). There have also been suggested functional forms fitting $\log \tau$ vs. $T$ quite well in the measured range but that do not even imply the existence of any thermodynamic singularity below the glass transition temperature, but simply a powerlaw growth $((T - T^*)^{8/3})$ of frustration limited domain reconfiguration energy away from a second order-like transition at some temperature $T^* > T_g$ \[52\]. In general, many attempts to fit the viscosity data $\eta(T)$, including those mentioned above, generally assume an activation type expression $\eta(T) = \eta_0 e^{f(T)}$, where $\lim_{T \to \infty} f(T) \to 0$, and take both the prefactor $\eta_0$ and the numerical constants in the exponent $f(T)$ as adjustable parameters. Taking all those parameters as adjustable without theoretical prejudice is the main difficulty in obtaining an unambiguous interpretation.

Consider a simple VTF-like $\eta(T) = \eta_0 e^{DT_K/(T - T_K)}$ as an example. Assume also, for the sake of argument, that there were no (visually) satisfactory fit of experimental $\eta(T)$ data for a particular substance with a single VTF law. Let us then attempt to fit only some low $T$ portion of the data with the VTF (certainly, the RFOT theory says this should work close enough to $T_K$). Experience shows that small portions of experimental $\eta(T)$ data are smooth and featureless enough to be easily overfitted with a three-parameter VTF form. Furthermore, while smaller portions of the $\eta(T)$ data are increasingly easier to fit, the resultant values of the fitting parameters attain increasingly more
unphysical values. Most notably, $\eta_0$, bearing the meaning of the high temperature viscosity, will dramatically differ from its empirical value, known to be of the order a centipoise for all substances near their boiling temperature. Consequently, in our view, one should not trust the corresponding values of $T_K$ and $D$ obtained in such a fit. It is our impression that most (but not all) workers that have used the concepts of fragility and $T_K$ as fitting parameters are aware of this point. Some other ways of analyzing the relaxation times, such as using the concept of fragility index \cite{54, 55} partially avoid dealing with the prefactor $\eta_0$ explicitly, but have the potential to hide an unphysical $\eta_0$. On the other hand, if the value of $T_K$ and the preexponential factor $\eta_0$ are independently known, the resultant fits, although not visually perfect will yield more physical outcomes. As far as the value of $\eta_0$ is concerned, the RFOT theory is specific in that it requires that in the predicted $\eta(T)$ from $\tau(T) = \tau_0 \exp(32./s_c)$, $\tau_0$ be equal to the mean molecular flight time, or equivalently at these temperatures, a few molecular vibrational times. As a result, the RFOT prescribes that the activated contribution to the viscosity should equal $\eta(T) = \eta_0 \exp(32./s_c)$, where $\eta_0$ is indeed the high temperature/low density viscosity of the liquid, which could be measured experimentally on short time scales or calculated by a perturbative extension of the standard kinetic theory of a dilute gas in the manner of Enskog. Clearly, since the activation barriers at $T_A$ vanish, the main source of molecular drag near $T_A$ will come from the multiple collision dynamics described by the Mode Coupling Theory and which is not addressed in this paper. Still, activated transport dominates at low temperatures, when the viscosity exceeds a few poise for simple liquids. This number would need to be modified for polymers where we know long relaxation times of the chain can come in even for dilute solutions owing to the Rouse modes \cite{37}. The discussion above suggests that we employ the following fitting procedure that is free of the overfitting problems just mentioned and that only uses the RFOT predictions in the regime of their presumed applicability. Suppose we have experimental viscosity and configurational data for a substance between its glass transition and the boiling temperatures. The activation contribution to the viscosity is presented as $\eta(T) \equiv \eta_0 \exp(F^\dagger/T)$, where the barrier $F^\dagger$ is computed using Eq. (10), using the experimentally observed $s_c$ and some value of $T_A$, that in the end will be our fitting parameter. The value of $\eta_0$ is not computed by the RFOT theory but is known to be within a factor of two or so to to equal the high temperature value of viscosity, although in fact it should be somewhat density dependent owing to the collision rate dependence on density. Isochoric measurements of transport properties are much needed and should be easier to interpret! To avoid ambiguity, we will take $\eta_0$ equal exactly the viscosity of the liquid at the boiling point. The slight looseness of this procedure can only result in a logarithmic error to the exponent itself, that we focus on in this work. Recall that the $s_c$ in formula (3) is measured per independently moving molecular unit (or, more concisely, per one “bead”). The bead count will be presented for all four substances we consider in this paper, however we can be sure of its exact value only within say 30% accuracy, with the degree of uncertainty being
smaller for simple liquids and larger for bigger molecules as we will discuss below. Empirically, the temperature dependence of experimentally inferred configurational entropy follows very well the following functional form \[15\]: \[ s_{c}^{\text{exp}} = s_{\infty}(1 - T_{K}/T). \] (Here, the experimental input \( s_{c}^{\text{exp}} \) is indicated per mole, not bead!). Obviously, the parameter \( s_{\infty} \) would be equal to the heat capacity jump at the ideal glass transition temperature \( T_{K} \); while at the arbitrary temperature \( T \) the jump is \( \Delta c_{p}(T) = s_{\infty}(T_{K}/T) \). We will not fit with respect to \( T_{K} \), but take it from the experimentally determined \( s_{c}(T) \) to avoid the overfitting mentioned earlier. However, since \( s_{\infty} \) is known directly only on a per mole basis, we find it convenient to treat the overall factor for \( s_{c} \) in Eq.(10) (remember this one is per bead!) as a fitting parameter. We call this parameter \( s_{\text{fit}} \), it is therefore the fitted prefactor of the configurational entropy per bead: \( s_{c}(T) \equiv s_{\text{fit}}(1 - T_{K}/T). \) Now, if we knew exactly the number of beads to be assigned per molecule (which we call \( b_{K} \)), we could then directly compare quantity \( s_{\infty}/b_{K} \) with \( s_{\text{fit}} \) in order to assess the quality of our approximations. The ratio \( (s_{\infty}/b_{K})/s_{\text{fit}} \), reflecting the degree of deviation of the theory from the experiment can be presented more conveniently as \( (s_{\infty}/s_{\text{fit}})/b_{K} \) - that is as the ratio of the bead count \( s_{\infty}/s_{\text{fit}} \) predicted by the RFOT theory (within current approximations!) and our à priori bead count, to be discussed below, in due time. In an ideal situation, where the bead count approach is exact, the value of \( (s_{\infty}/s_{\text{fit}})/b \) would be equal to one. We should mention that in our minds the “bead” concept does not refer to some arcane renormalized object but merely recognizes that almost all the substances treated here are made up of aspherical molecules not hard spheres, so the calculation of the interface tension refers to the localization of the quasispherical parts of each such molecule. It would be much clearer, if RFOT could be discussed in the context of molten salts or other mixtures of spherical components, but all the relevant data for a test do not seem to be available for these systems. An independent theoretical soundness check is that both the fitted and the experimental value of \( s_{c} \) per bead near \( T_{g} \) should be on the order of the universal .82 predicted by the vanilla version of the RFOT theory for all substances at a glass transition on one hour time scale (although a deviation is expected, and more so for substances with \( T_{A} \) and \( T_{K} \) closer to each other). A deviation of the quantity \( s_{\infty}/s_{\text{fit}} \) from unity could, in principle, happen for four (mostly independent) reasons: first, a possible inaccuracy of the RFOT estimate of the droplet surface tension owing to a more complicated interface structure; second, an incorrectly estimated bead count (the number of beads per molecule of the substance); third, the approximate nature of the argument leading to Eq.(10); and final fourth, an uncertainty in experimental estimation of the configurational entropy \( s_{c} \) owing to different vibrational properties of crystals and aperiodic structures (this is discussed in some detail in \[43\], see also \[43\]). We have already commented on the approximations of the softening anzatz from Eq.(10), however we would like to say a few words in connection with the first two possible sources of error. The determination of the factor “32.” in Eq.(3) for simple liquids uses no hidden assumptions and would be expected to be accurate within no worse than a factor of
Moreover this constant should be nearly the same for all those substances owing to the near universal Lindemann parameter. At the same time, polymeric molecules may exhibit effects of a finite chain persistence length which is often hard to determine. Clearly, close enough to $T_K$ the persistence length will be smaller than any relevant length scales in the problem, however just above $T_g$ the critical droplet radius following from Eq. (1) is still only $2.3a$, suggesting a possibility of microscopic effects. Physically, persistence length phenomena will lead to a larger effective bead size and thus are hard to separate from the bead count issue. Additionally, polymeric substances often have beads of very different size (see below), therefore using a single generic bead size $a$ probably introduces another source of quantitative discrepancy. More importantly, polymers may exhibit local ordering transitions, such as crystallization or orientational ordering that fail to grow to detectible size because of entanglement. These effects are clearly not included in our present analysis, not to mention the effects of the existence of very long time relaxation processes in polymer melts even in the absence of supercooling. A separate theory for these effects is needed to achieve a quantitative description of relaxation in liquids comprised of very long molecules. To finish the discussion of the choice of fitting parameters, we mention another reason why we use the entropy coefficient as a fitting parameter rather than, say, the fragility $D$ from the VTF. Due to the empirical temperature dependence of the configurational entropy $s_c \propto (1 - T_K/T)$ - a plain AG law does not precisely follow the appropriate functional form even in the absence of softening. Instead, the bare RFOT predicts a slightly different $\log(\eta/\eta_0) = D_1 T/(T - T_K)$, as compared to the VTF’s $\log(\eta/\eta_0) = D T_K/(T - T_K)$. While asymptotically these two forms are equivalent as $T \to T_K$, the exact numerical value of the “fragility” factor $D_1$ will differ from the standard fragility $D$ at $T_g$ by a factor of $T_K/T_g$, which can be significantly different from unity ($\sim 1/2$ in the case of a-Silica).

We have chosen four substances - silica, 1-propanol, tri-naphthyl benzene (TNB) and salol - to demonstrate our theoretical conclusions. This particular choice was suggested by the following rationale. First, thermodynamic data are available for these materials; second, these substances cover a wide range of fragility values, with silica being the strongest substance, TNB and salol the most fragile and propanol being in the intermediate range. From an RFOT theoretical perspective TNB and salol are also attractive because of their being notorious for deviating from the plain VTF dependence; besides, the length scale of RFOT theory has been checked for TNB [12]. The experimental points and the fitted curves are shown in the l.h.s. panes of Figs. 4-7. The corresponding parameter values are shown in Table 1.

The r.h.s. panes of Figs. 4-7 show the temperature dependence of the relevant length scales for each respective substance. The thicker lines denote the critical radius $r^\dagger$ (solid) and the cooperativity length $\xi$ (dashed) in units of molecular length $a$. The corresponding thin lines show what those
length scales would be in the bare RFOT theory without softening $r^*/a$ from Eq. (5) and $\xi/a$ from Eq. (6). Note, the configurational entropy, used to compute the length scales with and without softening are taken from the fitted value of $s_{fit}$, calculated with softening, to allow for direct comparison, that is to illustrate: “smaller barriers” ⇒ “smaller droplets”. Fitting the viscosity data with a plain VTF would result in a slightly different bare value of $r^*$ and $\xi$. In fact, while the precise $s_c$ at $T_g$ is sensitive to whether softening effects are included, the length scales near $T_g$ (but not immediately near $T_A$) are not very sensitive (we make comments in this later on).

We remind the reader that $T_K$ and $\eta_0$ were fixed by independently measured thermodynamics and the measured viscosity near boiling respectively; on the other hand $T_A$ and $s_{fit}$ were varied to fit the low temperature part of the $\eta(T)$ curves only. Since $T_K$ is not varied (from its thermodynamic value), the outcome of the fitting procedure is rather insensitive to the exact choice of the low $T$ fragment of the data used for fitting. For clarity, we used all experimental viscosity data above 10 poise in the fit (and at $T > T_g$). This is internally consistent within the theory, as will be shown soon when analyzing the derived critical droplet sizes (those should be at least one molecular length $a$). Using fewer high $T$ points results in a somewhat higher value of $T_A$, but the change in its value is not dramatic. Lastly, in the case of Silica, the high $T$ value of viscosity at the vaporization point is not known (surprisingly, its boiling point itself is not known well either), therefore we took (admittedly arbitrarily) $\eta_0$(a-SiO$_2$) = 1 centipoise.

Let us inspect the fitted theory versus experiment graphs in Figs. 4-7. With the exception of silica, whose data simply do not extend into high enough temperatures, all figures demonstrate that there

| substance | $T_g,K$ | $T_K,K$ | $s_\infty,k_B$ | $\eta_0,cPs$ | $T_m$ | $s_\infty(T_m-T_K)/T_m$ | $\Delta H/T_m$ | $T_A,K$ | $s_{fit,k_B}$ | $s_\infty/s_{fit}$ |
|----------|---------|---------|----------------|---------------|-------|----------------------|----------------|---------|----------------|------------------|
| Salol    | 220     | 175     | 16.7           | 1.16          | 315   | 7.4                  | 7.34           | 333     | 2.65           | 6.29             |
| TNB      | 342     | 271     | 25.14          | 1.1           | 472   | 10.7                 | 10.8           | 561     | 2.68           | 9.37             |
| 1-Propanol | 97.0    | 72.2    | 8.53           | 0.41          | 146   | 4.31                 | 4.87           | 252     | 2.89           | 2.95             |
| a-Silica | 1480    | 876     | 1.49           | 1.0           | 1700  | .72                  | 0.66           | 5960    | 1.90           | 0.78             |

Table 1: First five columns give known quantities (Ref. [45] for salol and propanol; Ref. [46] for TNB, Ref. [47] for a-Silica). Columns six and seven demonstrate consistency between the used form of the configurational entropy (provided by other workers, as cited) and the known value of the enthalpy of fusion. Indeed, by definition of configurational entropy ($s_c = s_{liq} - s_{cryst}$): $\int_{T_K}^{T_m}(\Delta c_p/T)dt = \Delta S_m \Rightarrow s_\infty(T_m-T_K)/T_m = \Delta H/T_m$, if one uses the empirical form $s_c = s_\infty(1 - T_K/T)$. Additionally, these numbers give an idea how many independent moving units are in each molecule of the substance, if one adopts the view that a fixed amount of entropy per such moving unit is lost at freezing (see the extended discussion in the last section). Next two columns show the fitted values of $T_A$ and $s_{fit}$ respectively. The ratio $s_\infty/s_{fit}$ is a quantity that, within RFOT, should give the effective number of beads per molecule, as expressed by the rate of entropy loss at $T_K$. 


Figure 4: Experimental data (symbols) for salol’s viscosity (Ref. [48]), superimposed on the results of our fitting procedure (line) are shown. $T_A$ is shown by a tickmark. The r.h.s. pane depicts the temperature dependence of the length scales of cooperative motions in the liquid. The thick solid and dashed lines are $r^\ddagger$ and $\xi$ respectively (see text). The thinner counterparts show what those lengths would be in the bare RFOT, but calculated using the same value $s_{fit}$ as the renormalized lengths (this comparison is only of limited value, because, remember that the value of $s_{fit}$ that should be used to calculate $r^\ddagger$ and $\xi$ in the absence of softening would be different from the one computed with softening. Experience shows, the values of the length at $T_g$, unlike $s_c(T_g)$, is rather insensitive to whether softening is present or not).

exists temperature ($T_A$) above which the barrier for activated motions in the liquid disappears. This is the temperature at which the fitted log-viscosity begins to level off. We remind the reader that only the activated part of the viscosity has been computed in this work. Clearly, this activated mechanism becomes subdominant at viscosities below 10 poise or so, where the experimental and the curves fitted to the low temperature data begin to diverge. With remarkable consistency among all substances considered, this divergence temperature (call it $T_{cr}$) coincides with the temperature at which the critical (transition state) droplet radius equals the molecular size $a$ (see the r.h.s. panes of Figs. 4-7). We see therefore the RFOT theory provides an internal criterion for when it should fail to quantitatively account for the relaxation rate values - obviously, the critical droplet size cannot be smaller than a molecule’s size (within a factor of order unity, of course; this factor, encouragingly, is consistently around unity among the few materials analyzed here. To avoid ambiguity, we define $T_{cr}$ as the temperature at which the value of the critical radius $r^\ddagger$ is strictly equal to the molecular length scale $a$, although other conventions are possible). While the equations described here do give results between $T_A$ and $T_{cr}$, clearly a continuum treatment in this size regime is suspicious since $r^\ddagger$ is less than a particle size. It makes sense in this temperature range to invoke a thoroughgoing single particle picture of the activated events. Very promising work by Schweizer and Saltzman [56].
Figure 5: Same as Fig.4 but for TNB. Experimental data are taken from Ref. [49].

along these lines appeared just as this paper was finished. They use a quantity similar in spirit to our $\Delta f$ to estimate the barrier for a single particle to escape its cage, which should be adequate in this regime.

Our result that the crossover between activated and collisional transport should take place at a specific time scale or viscosity is consistent with recent experimental findings in [57] on the pressure dependence of relaxation times in several materials, where there was observed a crossover between two types of the pressure dependence of the dielectric response, similar to what is seen in the $\log(\eta(T))$. As expected, at higher temperatures this crossover occurs at higher pressures. Remarkably though, the crossover takes place at the same value of the relaxation time! This is a clear indication that this transition has to do with excluded volume effects, consistent with our conclusions that for $T > T_A$ the collisional viscosity mechanism dominates. The temperature $T_{cr}$ of the crossover between collisional and activated transport corresponds well to the purely empirically defined break temperature $T_B$, at which the Stickel’s [51] $[d \log \tau/d(1/T)]^{-1/2}$ vs. $1/T$ plot exhibits a visible kink (see also [58]). We have noted in the previous paragraph that there is a degree of uncertainty about the value of the prefactor $\eta_0$ for Silica, whose $T_A$ is rather high which indeed turns out to be above its boiling point. Obviously, quite an extrapolation is involved. Nevertheless, we note that the crossover temperature $T_{cr}$ at which our theory predicts a crossover between activated and collision dominated transport mechanisms is about 3700 K for silica. This is consistent with the simulations of Horbach and Kob [53], who recover a transition to dynamics characteristic of fragile liquids at a temperature $T_c = 3330$.

As we have just seen, taking into account droplet interface softening reveals that the critical tran-
1-Propanol

Figure 6: Same as Fig. 4, but for propanol. Experimental data are taken from Ref. [48]. Note, viscosity points for this substance are available in a more narrow range than, for example dielectric relaxation; in fact the data stop at a temperature significantly above the conventional $T_g$. Nevertheless, we prefer to use the viscosity measurements do reduce ambiguity in the prefactor (see text). The fitted log(τ(T)) in the region of no experimental data should in fact be considered as a prediction of the RFOT theory.

Transition state droplet size $r^\dagger$ is smaller than expected otherwise from the bare version of the RFOT. This is demonstrated in the r.h.s. graphs of Figs. 4-7. The effect is more pronounced for substances with a smaller value of $T_A/T_K$ ratio. This ratio, as we have mentioned earlier, gives the relative value of the relevant energy scales at the dynamical and ideal glass transition. The fitted value of $T_A/T_K$ for the two most fragile substances is about 2.; the intermediate fragility substance has a fitted $T_A/T_K$ of 3.5 and silica a value of 6.8. According to the work of Hall and Wolynes [59], this ratio reflects the degree of network formation in the substance. The Hall-Wolynes prediction for interacting spheres with a pure $r^{-12}$ repulsion gives $T_A/T_K = 1.3$ while the ratio is predicted to be much larger for silica, but of course the effect of vaporization was not included in that work. A relative decrease of the softened critical radii is a consequence of the barrier vanishing at the dynamical transition temperature $T_A$, as explained in the previous section.

Let us now see quantitatively how the barrier height is lowered when mode softening is included in the theory. The ratio of the renormalized barrier to its $T_K$-asymptotic form $F^\dagger/T = 32./s_c$, calculated in [3], is shown in Fig. 8. The graph in Fig. 8 is designed to show how the prediction of the $T_K$-asymptotic RFOT theory is modified when the barrier vanishing at the spinodal $T_A$ is included in the treatment. This more complete theory, albeit approximate, explicitly shows that the barriers for droplet rearrangements must disappear at some temperature, that we have called $T_A$. Of course, since the critical droplet size is smaller than one molecular length at a temperature
still lower than $T_A$, the precise calculated value of the barrier at this point should not be taken too seriously. The theory nevertheless predicts that at temperatures above $T_{cr}$ the $\alpha$-relaxation barriers have reached their lowest possible value, and a collisional mechanism becomes the main contributor to the liquid’s viscosity. On the other hand, the barrier renormalization becomes less significant as one approaches $T_K$, the softening effects should vanish, subduing themselves to the singularity at $T_K$. At $T_g$, however, this renormalization is still quite noticeable, as represented by the relative barrier value less than one. This renormalization coefficient also has additional significance in that it tells one how the apparent fragility of a given substance would differ if one were to use the softening anzatz from Eq. (10) as opposed to the bare RFOT’s Eq.(1) (this in addition to the factor $T_g/T_K$ that may arise depending on which functional form of $s_c(T)$ is used, as mentioned earlier).

At this point in the discussion, judging from the four analyzed substances, a pattern emerges that stronger substances tend to have a larger value of $T_A/T_K$ ratio. As mentioned, this was explained in [59] by a varying degree of bonding in the various liquids and indeed conforms to the lore that stronger substances tend to form a larger number of directional bonds per molecular unit.

2.1 Das Glasperlenspiel

We have already mostly discussed the implications of the appearance and significance of the temperature $T_A$ for interpreting the features seen in plot of log $\eta(T)$. Let us now check whether the predictions of the entropy per bead needed for RFOT fits actually matches our structural and
Fig. 8: Shown here are the ratios of the softened relaxation barriers (from Eq. (10)) to their bare values, calculated using Eq. (1) and $s_c = s_{fit}(1 - T_K/T)$.

thermodynamic expectations (the results of the following discussion are summarized in Table 2). We phrase the issue of comparing microscopic theory and experiment in this way because of the manner of the fit we have used and possible ambiguities in defining $s_c$ (per bead). One could equally well argue that it is the bare surface tension argument that is in error in the RFOT theory so the surface tension should be modified. In fact variations of less than 50% in the bare surface tension give nearly equivalent effects to changes in $s_c$. In order to conduct this comparison of microscopic theory and experiment, we must determine the number of beads for each material. First, there is a procedure based on an intuitive parsing of the molecular structure: salol consists of two benzene rings connected by a carbonyl and an oxygen - hence it should have 4 beads (a benzene ring is a rigid entity). TNB (tri-naphthyl benzene) consists of three naphthyl groups (effectively double benzene rings) connected by a benzene - giving a count of 7 beads (we count a naphthyl as having two beads in spite of its rigidity because it has a rotational degree of freedom around the out-of-plane symmetry axis). Propanol, we would say, has three beads (the OH group is hydrogen bonded to a neighbor). Silica is a difficult case because it is hard to estimate the degree of independence of silicon and oxygen atoms in this highly networked substance which some may consider a molten salt. Notwithstanding this ambiguity, we assume here one bead per molecule (there is indeed one oxygen per tetrahedron, which is, apropos, often thought to be the moving unit in a-SiO$_2$ [60]). As seen from Table 2 the results are quite reassuring, with the largest disagreement between molecular structural intuition and RFOT theory with softening being 57% for salol. Remember, there are at least four independent sources of error potentially contributing to this discrepancy, as discussed earlier.

Now, admittedly, the bead assignment procedure has an element of subjectivity. (Ways of pre-
Table 2: The first column repeats the last column of Table I, this would be the exact bead count for these substances, if both $s_\infty$ and $s_{fit}$ were determined precisely. Next six columns are organized into three pairs. In each pair, the first number gives the bead number estimated by a particular method (see text) and the resultant ratio of the heat capacity jump at $T_K$ per bead determined from this bead count to the same quantity as obtained in the fit. $b_{HS}$ denotes the bead number per molecule calculated using the entropy of melting of a hard sphere liquid $s_{HS} = 1.16k_B$. $b_{LJ}$ is the same quantity but estimated using the entropy of melting of a Lennard-Jones liquid $s_{LJ} = 1.68k_B$.

| substance | $b_K \equiv s_\infty/s_{fit}$ | $b_{chem}$ | $b_K/b_{chem}$ | $b_{HS}$ | $b_K/b_{HS}$ | $b_{LJ}$ | $b_K/b_{LJ}$ |
|-----------|-------------------|---------|----------------|--------|---------|--------|----------------|
| Salol     | 6.29              | 4       | 1.57           | 6.32   | 1.00    | 4.36   | 1.44           |
| TNB       | 9.37              | 7       | 1.34           | 9.33   | 1.01    | 6.44   | 1.46           |
| 1-Propanol| 2.95              | 3       | 0.98           | 4.20   | 0.70    | 2.90   | 1.02           |
| a-Silica  | 0.78              | 1       | 0.78           | 0.57   | 1.37    | 0.39   | 1.99           |

Table 3: The first column lists the values of configurational entropy per bead at the glass transition temperature $T_g$ as derived from our fits: $s_c(T_g) = s_{fit}(1 - T_K/T_g)$. These are to be compared to the experimental values of $s_c^{exp}$ at $T_g$ per bead obtained according to $s_c^{exp}(per\ bead) = s_\infty(1 - T_K/T_g)/b$ using a bead count $b$ estimated by a particular method (see text). A useful reference value of $s_c$ is 0.82, predicted to hold universally at $T_g$ on the one hour time scale by the RFOT theory without softening.

| substance | $s_c^{theor}(T_g),k_B$ | $s_c^{exp}(chem),k_B$ | $s_c^{exp}(HS),k_B$ | $s_c^{exp}(LJ),k_B$ |
|-----------|--------------------------|------------------------|---------------------|---------------------|
| Salol     | 0.54                     | 0.85                   | 0.54                | 0.78                |
| TNB       | 0.56                     | 0.75                   | 0.56                | 0.81                |
| 1-Propanol| 0.74                     | 0.73                   | 0.52                | 0.75                |
| a-Silica  | 0.78                     | 0.61                   | 1.0                 | 1.54                |
senting the thermodynamics near $T_g$ in a bead count independent fashion have been used before (see for example [42][62]). We may therefore propose a completely automatized, interpretation free procedure, that uses measurable data on the entropy of crystallization. The motivation for this is that, clearly, a similar issue of bead counting would arise if we tried to describe freezing of a molecular liquid by comparison with a theory for atomic entities that are spherical. Fortunately for us in making this comparison, all four substances exist in crystalline form (actually, more than one crystalline form for silica, where we will use the low $T$ quartz polymorph). In the RFOT theory, the precise meaning of a bead is that it should effectively behave as a hard sphere in terms of its entropy loss in the ideal localized state at $T_K$ and as the elementary unit of a droplet-droplet interface. From the entropy point of view a similar localization also occurs at freezing. We may therefore estimate the number of (hard sphere) beads in a particular molecule by dividing the entropy of fusion of this substance by the entropy of fusion of a hard sphere (HS) liquid, known to be $s_{HS} = 1.16k_B$ [63], that is bead$# = (\Delta H/T_m)/s_{HS}$. Obviously, crystallization and vitrification are different in several ways. For example, the freezing occurs with a volume change ($\sim 10\%$ for a hard sphere liquid) while the glass transition does not have a volume change. Thus freezing will have a larger dependence on the attractive forces. Hence, an alternate bead count may also take into account the attractive force changes (the Lennard-Jones (LJ) liquid’s entropy of fusion is larger than that of a hard sphere liquid. We assume it is equal to the fusion entropy of argon $s_{LJ} = 1.68k_B$, which is indeed a nearly LJ substance [61]); similarly, the softness of the core potential for metals enters into their fusion entropies. We should not be surprised to find therefore a deviation from the hard sphere estimate, but for chemically similar systems there will be a more or less systematic deviation. Notwithstanding these caveats, the procedure now has the merit of being totally unambiguous. The results of counting beads by using both the freezing entropy of a hard sphere and a Lennard-Jones liquid are also presented in Table 2. We see that our earlier conclusions still hold, at least for these four substances. We note it is important that both the glass and crystal have no remaining degrees of freedom i.e. freezing does not produce plastic orientationally disordered crystals.

Still, can we independently verify that using bead$# = (\Delta H/T_m)/s_{HS}$ is reasonable more generally? We have found several reassuring signs that the answer is affirmative. Consider plotting the kinetically estimated fragility index $m$ versus the following quantity $m_{calc} = cT_g\Delta C_p/\Delta H_m$, as done by Wang and Angell in [62]. $\Delta C_p$ and $\Delta H_m$ are heat capacity jump at $T_g$ and $\Delta H_m$ is the fusion enthalpy, both per mole, not per bead. Clearly, Wang-Angell plots successfully avoid the issue of how many independently moving units a molecule should be considered to have. Empirically, they observed a correlation between the kinematic $m$ and $m_{calc}$ (Fig.1 of [62]). If one draws a line through the densest linear cluster on the $m$ vs. $m_{calc}$ graph (which appears to edge the total cluster), numerical value 56 for the slope $c$ fits well. However values of $c$ up 70 seem to be still
consistent within the scatter of the data, if all points are given equal weight. On the other hand, we can qualitatively estimate the value of $m_{\text{calc}}$ as predicted by the RFOT. Assume for the sake of argument that the VTF in the vanilla form from RFOT of $\tau = \tau_0 \exp(32./s_c)$ (as follows from Eq. (3) holds (this is indeed a good approximation for many substances). Additionally, assume the empirical form of the configurational entropy, that we have used throughout the paper: $s_c = s_\infty(1 - T_K/T)$ [45]. We have seen the latter expression is indeed a very good approximation. The corresponding (temperature dependent) heat capacity jump is then $\Delta c_p = \Delta c_p(T_g)(32./s_c(T_g)) \log_{10} e$.

With our proposed way to estimate the bead count from the fusion entropy, the heat capacity per bead $\Delta c_p$ is then $\Delta c_p = \Delta c_p(s_{HS}T_m/\Delta H_m)$. Finally, within bare RFOT,

$$m = \frac{T_g \Delta c_p(T_g)}{\Delta H_m} \left\{ s_{HS}(\log_{10} e) \frac{32.}{s_c(T_g)} \frac{T_m}{T_g} \right\},$$

where we remind the reader $s_c(T_g)$ is a per bead quantity corresponding to the effective hard sphere model. The ratio $T_m/T_g$ is almost universally 3/2. Using the value $s_c(T_g) = .82$ at the hour scale and $s_{HS} = 1.16$, the numerical factor in the curly brackets (corresponding to $c$) is $\approx 36..$ If one were to use the Lennard-Jones fusion entropy $s_{L,J} = 1.66$ rather than $s_{HS}$ in this expression, the numerical factor $c$ predicted for the Wang-Angell plot is about 52, rather close to the Wang-Angell value. Additionally, note that the real $s_c(T_g)$ tends to be a bit smaller when softening effects are included. Finally, we note that in applications it may be beneficial to remember that ratio $T_g \Delta C_p/\Delta H_m$ depends only on the ratio of $T_m$ to $T_K$ (see the caption to Table 1):

$$\frac{T_g \Delta c_p(T_g)}{\Delta H_m} = \frac{T_K}{T_m - T_K}.$$  

(12)

It appears a useful exercise to assess the quality of both our fitting method and the bead number assignment by looking at the values of the configurational entropy at $T_g$ per bead as extracted from the theoretically computed $s_{fit}$ and from the experimental number $s_\infty$ divided by our à priori bead count (see Table 3). While all numbers appear to be reasonable (and in fact comparable to the bare RFOT’s $s_c(T_g) = 0.82$), only the Lennard-Jones bead count for silica, again, seems too low, consistent with our earlier findings.

In fact, we note, the comparison of glass physics with the fusion entropy is quite venerable being intrinsic to Kauzmann’s way of plotting the configurational entropy as function of temperature, divided by entropy loss $\Delta s_m$ during crystallization, again a “bead” independent quantity. At $T_g$, the plain RFOT and $s_{HS} = 1.16$ predicts $s_c/s_m \sim .82/1.16 \simeq .7$ (this falls within the range of observed values. See a compendium of experimental values of $s_c/s_m$ for polymers (both entropies per mole), given in [50]). As we have seen, with softening included, $s_c(T_g)$ is not a constant and seems to range from $\sim .5$ to $\sim 1$ (see Table 3). Curiously the smallest value of this quantity reported
in is \( \sim 0.1 \) for PVC. We suspect this exceptionally low apparent value of the configurational entropy at \( T_g \) may well be caused by partial crystallization that goes unnoticed because it occurs locally and over a range of different temperatures due to heterogeneity in local environment.

One observes that the values of \( s_{fit} \) are apparently remarkably close to each other. Therefore, the heat capacity jumps, as they would be at \( T_K \), will be much closer in magnitude than the apparent experimental \( \Delta c_p \)'s at \( T_g \), which differ at least by an order of magnitude (note, our substances cover a good range of fragilities that have been encountered so far). This notion supports, albeit circumstancially, the usefullness of the concept of a “bead” as a reference motional unit in a glass. It seems, structural degrees of freedom as expressed in terms of motions of the beads appear to have much more in common, even quantitatively, in spite of apparent chemical idiosyncrasies of different materials. Nevertheless, nothing in the theory so far insists that \( \Delta c_p(T_K) \) per bead should be the same for all substances. Remember, the size of the bead \( a \) (that would affect the bead count), enters in the theory in two (what so far seems) largely independent places. On the one hand, it is the reference length scale in the argument on the surface tension coefficient \( \sigma_0 \); on the other hand, it determines the volume density of beads as derived from the configurational entropy data.

One can appreciate some of these points graphically by plotting \( \log[\eta(T)] \) versus \( T_g/T \) and \( T_K/T \), as shown in Figs. 9 and 10 respectively.

![Figure 9: Shown is the Angell plot of the log-viscosity data as a function of \( T_g/T \). The symbols denote experimental points. The lines are our the RFOT results (shown only between \( T_A \) and \( T_g \)).](image)

Note that the easily visible difference in slopes between the curves when viscosity is plotted vs. \( T_g/T \), become rather less pronounced in the \( T_K/T \) graph. According to the present theory, some of the differences in the qualitative behavior of the \( \log(\eta) \) temperature dependence are due to varying degree to which the softening effects play a role at the glass transition. This degree is
Figure 10: Theoretical log-viscosity curves as functions of $T_K/T$ (shown only between $T_A$ and $T_g$).

directly related to the ratio of the two basic energy scales in the theory: $T_A$ and $T_K$. According to RFOT, $T_K$ gives the energy scale of the ideal glass transition, below which structural equilibration is impossible in principle. $T_A$, on the other hand gives a reference energy at which the liquid would fall out of equilibrium, if activated events were eliminated as in mean-field theory. The glass transition temperature $T_g$, in contrast, bears no fundamental meaning, but only reflects the amount of patience of the experimenter. We suggest that plotting the log-viscosity data as a function of $T_K/T$ (with thermodynamically derived $T_K$) will make it easier to separate to some extent the phenomena characteristic of the ideal glass transition from those occurring near the onset of activated transport.

3 Discussion and Conclusions

The RFOT theory of supercooled liquid dynamics differs from a pure ”entropy” theory by exhibiting the phenomenon of barrier softening as the spinodal or mode coupling temperature $T_A$ is approached from below. We have shown here that an approximate theory of these softening effects indeed accounts for the deviations from the VTF law that experimentalists have previously noticed.

From a formal point of view, the present treatment of the barrier softening is not complete, especially by not being symmetric about $T_A$. Above $T_A$, if the naive MCT relaxation time is sufficiently long, activated events can short circuit the predicted singularly slow relaxation from MCT. Likewise, additional mode coupling effects may play a role just below $T_A$. Treating this feature is a problem for future work. We feel that it concerns, on a logarithmic scale, only a small part of the dynamic range from a few centipoise to a few decapoise, a small fraction of the range of viscosities explored in
the laboratory. This is however the range most easily addressed by computer simulation currently so further work on the problem is warranted.

We also comment that in this paper we treat two quantities that enter the theory as independent, one $\Delta c_p$ (at $T_g$) and the other the ratio $T_A/T_K$. Yet the curve fits show these two quantities clearly are correlated (empirically so far). Indeed in some detailed microscopic models the quantities are correlated too. Hall and Wolynes’ calculations suggest they are both functions of the fraction of bonds that are made in a model network liquid. Yet the Hall-Wolynes treatment suggests they should also be functions of the detailed force laws as well. Thus there may be ways of teasing the two features determining fragility apart by a judicious choice of systems e.g. liquid metals. It is also possible that the correlation may arise from some common mechanism of frustration in many glasses, like icosahedral order formation in flat three dimensional space. In this case finding systems that break the correlation in the laboratory will prove difficult.

As to the molecular structural details it is perhaps remarkable that the RFOT theory does as well as it does. Indeed we see RFOT theory encounters strong parallels with the difficulties faced in the molecular theory of crystallization. Perhaps some of the complexities of that problem, polymorphisms and residual ordering transitions in the solid state (plastic crystallinity) are ameliorated here because they actually enter in only a statistical rather than a state specific way for glasses. In any event we note that the assumption of hard sphere geometry is by no means required by the RFOT theory approach which can make use of density functional methods to treat molecular network systems as has already been done to some extent. Such more detailed free energy functional models can be used to predict barriers by again constructing spatially inhomogeneous solutions of the appropriate molecular density functional corresponding with entropic droplets.

The barrier softening effects on the predicted length scales of dynamical heterogeneity are very modest near $T_g$. Because of this those predictions of the RFOT theory that are sensitive to length scale like the degree of non-exponentiality and density of the two-level systems are only moderately affected. Indeed since the lengths are a bit smaller that the vanilla RFOT, the Kohlrausch $\beta$ correlation between theory and experiment should improve (i.e. less dispersion of relaxation times). The lengths do decrease faster as $T$ increases from $T_g$ than they do in vanilla RFOT theory and this is consistent with the temperature dependence of violations of the Stokes-Einstein relation recently measured in TNB. Indeed the RFOT calculation with softening predicts no correction above the break temperature $T_{cr}$, in agreement with experiment.

In summary, this work has furthered the quantitative development of the random first order transition theory of the glass transition: First, we have computed how the activation barriers for structural relaxation in supercooled liquids are modified in the regime when the liquid is only
marginally supercooled, that is near to the so called dynamical transition temperature $T_A$. $T_A$ is in fact the temperature where alternative metastable liquid packings begin having statistical significance, as the liquid is cooled. Fluctuations of the order parameter at this dynamical transition at $T_A$ lead to vanishing surface tension between distinct aperiodic structures into which the liquid packs itself locally when supercooled. We call this droplet interface softening. As a result of this calculation, we have understood the significance of two distinct regimes in the relaxation time temperature dependence. The “diverging” low temperature part, represented by liquid’s viscosity above $\sim 10$ poise, indeed corresponds to local cooperative rearrangements, microscopically understood by the random first order transition calculation. Molecular transport in the higher $T$ portion, on the other hand, is dominated by a multiple collision mechanism, described by the mode-mode coupling theory, though strongly affected by the presence of activation, which is very facile at this point. Usually, the high temperature segment of the log $\tau(T)$ plot has been difficult to fit with the empirical VTF functional form. The theory makes clear that different mechanisms are responsible for molecular transport in systems at these different temperatures, as just explained. Our fitting of experimental data gives an unambiguous answer for the value of temperature $T_{cr}$ at which the crossover between the two regimes occurs. It also yields the value of $T_A$. We use the value of excess configurational entropy derived from calorimetry as input in the calculation. Finally, we compute the cooperativity length scales for structural relaxation in supercooled melts. While these length scales are around 5-6 molecular spacings at the glass transition, as predicted by the RFOT even without softening effects, they rapidly decrease upon warming and vanish at temperatures above $T_{cr}$.

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