The viscous slowing down of supercooled liquids as a temperature-controlled super-Arrhenius activated process: a description in terms of frustration-limited domains

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Abstract.   We propose that the salient feature to be explained about the glass transition of super-cooled liquids is the temperature-controlled super-Arrhenius activated nature of the viscous slowing down, more strikingly seen in weakly bonded, fragile systems. In the light of this observation, the relevance of simple models of spherically interacting particles and that of models based on free-volume congested dynamics are questioned. Finally, we discuss how the main aspects of the phenomenology of supercooled liquids, including the crossover from Arrhenius to super-Arrhenius activated behaviour and the heterogeneous character of the α-relaxation, can be described by an approach based on frustration-limited domains.

1. Introduction

What is there to be explained about supercooled liquids and the glass transition? The lack of agreement over the answer to this question certainly contributes to the multiplicity of proposed models and theories, many of which seem orthogonal to each other. Our own starting point, further motivated and discussed in this article, is that the most distinctive feature of supercooled liquids, in particular of the so-called 'fragile' liquids on which we focus, is the stupendous continuous increase of viscosity (η) and α-relaxation time (τ_α) with decreasing temperature (some 15-orders-of-magnitude increase over the range over which the substance is liquid, i.e., a factor-of-two change in temperature), an increase that is characterized for most liquids (with the possible exception of strong network-forming systems) by a crossover at a temperature T^* from a roughly Arrhenius temperature dependence of η and τ_α for $T > T^*$ to a faster-than-Arrhenius, or super-Arrhenius dependence for $T < T^*$. The viscous slowing down appears to be best described as a thermally activated process, whose evolution is primarily controlled by temperature and not by volume or density (at least at low pressure). It is of particular interest that the effective activation free energy for viscous flow and α-relaxation in *weakly bonded systems*, such as the much studied ortho-terphenyl, when measured relative to the energy characteristic of thermal fluctuations $k_B T$, varies by a factor of 5 or 6 between the melting point T_m and the glass 'transition' temperature T_g at which it reaches the high value of about 40, a value that is comparable to that of strongly bonded systems such as silica glasses. Concomitant with these variations and adding to the puzzle is the absence of associated singular behaviour or a strong signature in the structural data [1]. Whereas mounting evidence has been recently

provided that shows the slow dynamics in deeply supercooled liquids to be heterogeneous, with spatial heterogeneities (containing of the order of 10^2 molecules around T_g) being largely responsible for the nonexponential character of the α-relaxation and for the decoupling of translational diffusion timescales from viscosity and rotational relaxation times [1, 2], direct diffraction data do not seem to reflect the existence of supermolecular structural correlations. These are the phenomena that we find particularly intriguing as regards the glass transition, and our viewpoint is that models, theories, and computer simulations should be ultimately evaluated in terms of their ability to explain and describe these main features.

In the following, we first present some experimental evidence supporting the description of the viscous slowing down of glass-forming liquids as a temperature-controlled activated process crossing over to super-Arrhenius T-dependence in the supercooled regime. The emphasis is placed on weakly bonded, 'fragile' liquids. In the light of these observations, the relevance of simple atomistic models used in most computer simulations is addressed next. Finally, we summarize our theoretical approach to supercooled liquids based on frustration-limited domains and discuss its main ingredients and predictions.

2. The viscous slowing down as a T-controlled super-Arrhenius activated process

The dramatic increase of viscosity and α-relaxation time with decreasing temperature in supercooled liquids calls for a logarithmic representation that is traditionally displayed in an Arrhenius type of diagram, with $\log_{10}(\eta$ or $\tau_\alpha)$ as a function of $1/T$, or as advocated by Angell [3] as a function of T_g/T. As is already well known and is illustrated in figure 1(a), systems forming a network of strong intermolecular bonds such as GeO_2 are characterized by a rather linear variation in $1/T$, i.e., by an Arrhenius temperature dependence, while the other liquids show a marked upward curvature which represents a faster-than-Arrhenius, or super-Arrhenius, temperature dependence. This latter feature is particularly noticeable for weakly bonded, 'fragile' liquids, such as ortho-terphenyl [3]. A different way of presenting the phenomenon is to plot the effective activation free energy for a relaxation and viscosity, $E(T)$, specified by

$$\tau_\alpha = \tau_{\alpha,\infty} \exp\left(\frac{E(T)}{k_B T}\right) \tag{1}$$

where k_B is the Boltzmann constant and $\tau_{\alpha,\infty}$ is a high-T relaxation time taken as independent of temperature (a similar equation holds for the viscosity). This is illustrated in figure 1(b), where the temperature is scaled for each liquid to a temperature T^* above which the dependence is roughly Arrhenius-like, i.e., $E(T)$ is, to a good approximation, constant. The determination of T^* is subject to some uncertainty [4, 5], but the procedure stresses the crossover from Arrhenius-like to super-Arrhenius behaviour that is typical of most glass-forming liquids. A first observation is that $E(T)/k_B T$ is large compared to 1 (it is about 40 at T_g), which strongly suggests that the α-relaxation and the viscous flow in supercooled liquids are best described as thermally activated processes. The paradigm for an activated process is that of a chemical reaction where the activation barrier, typically more than $100 k_B T$, is reasonably independent of temperature (indicating an Arrhenius behaviour) and a reaction path involving a small set of coordinates may be well identified. Relaxation in strong network-forming systems, in which molecular transport requires that enough thermal energy be provided to break the strong intermolecular bonds, might be expected to fit this simple picture. However, the activated relaxation found in weakly bonded, fragile liquids is astonishing both because the effective activation free energy increases markedly as the temperature is lowered towards T_g (a factor of 3, or in units of $k_B T$ a factor of 6, in the case of ortho-terphenyl) and because it

reaches values that are much bigger than the typical energy associated with the intermolecular bonding. What are then the source and the explanation of this super-Arrhenius activated behaviour? They cannot be described by conventional transition-state theories used in the context of chemical reactions nor by standard theories of critical slowing down in the vicinity of a usual second-order phase transition. In connection with this last statement we note that the slowing down of dynamics when approaching a critical point (here, a hypothetical singular temperature below T_g as predicted for instance by the Vogel–Fulcher–Tammann formula) is usually characterized by a power-law growth of the relaxation time, which does not appear to fit the data on supercooled liquids with reasonable low values of the exponent. Unusually strong slowing down, with exponentially growing times, is however found near the critical point of some disordered systems like the random-field Ising model and is known as 'activated dynamic scaling [6].

An additional characteristic of the slowing down of the α-relaxation when approaching the glass transition is that it appears to be predominantly controlled by temperature and not by density. What is meant by this statement, and what are the consequences for potential theoretical explanations? Experiments on supercooled liquids are generally carried out at constant pressure, overwhelmingly at atmospheric pressure. As a result, a decrease of temp-erature also produces an increase in density (typically a 5% increase over the liquid range at $P = 1$ atm). The question is whether the dramatic slowing down and the above-mentioned crossover to super-Arrhenius behaviour observed at atmospheric pressure are primarily due to an intrinsic temperature effect or to the influence of density, and hence of packing. This can be answered by using pressure studies of α-relaxation and viscosity in glass-forming liquids. A pictorial way of addressing the problem is to plot $\log_{10}(\eta$ or $\tau_\alpha)$ as a function of $1/T$ at constant density ρ and as a function of ρ at constant T, for the range of densities that is relevant to the $P = 1$ atm phenomenon. An extensive data bank for these properties is not yet available, but some relevant pieces are. From the available experimental data, η and τ_α are seen to change typically by eight orders of magnitude along the isochores whereas a mere increase of one order of magnitude is observed along isotherms: see figures 2 to 5 of reference [7] and figure 4 of reference [8]. A detailed study of this phenomenon is given in reference [7]. One concludes that density seems to play a minor role compared to temperature, which indicates that the viscous slowing down of supercooled liquids, at least at low pressure, does not primarily result from a congestion mechanism such as described by hard-sphere models and simple free-volume theories.

3. Simple atomistic models versus real fragile glass formers

Liquid models involving one or two components of spherically interacting particles, such as the binary Lennard-Jones system, are the basis of many computer simulation studies and various approximate theoretical treatments. It is implicitly assumed that the characteristics of their viscous slowing down as temperature is lowered reproduce the main features of the phenomenology of real glass-forming liquids. We focus here on the ability of such models to describe the marked super-Arrhenius activated behaviour of α-relaxation and viscosity that, as stressed above, is a distinct property of real fragile supercooled liquids.

The most straightforward way to examine the relevance of the simple models is to plot the effective activation free energy $E(T)$ as a function of the scaled temperature T/T^*, or its inverse. To minimize bias, we use the values of $E(T)$ *and* T^* given by Sastry *et al* [9] in their study of the correlation between the properties of the inherent structures (potential energy landscape) and the slow relaxation. (Note that on the basis of their plot of $E(T)$ versus T/T^*, with $T^* = 1$ in Lennard-Jones reduced units, Sastry *et al* [9] pointed out that the binary
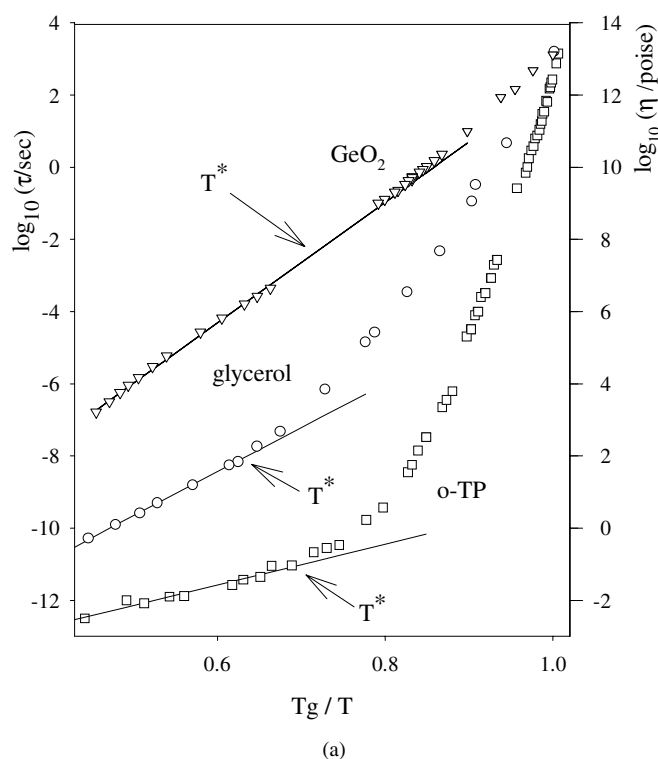
Figure 1. Super-Arrhenius T-dependence of the viscosity η and α-relaxation time τ_α in several representative glass-forming liquids. (a) The logarithm (base 10) of η and τ_α versus the reduced inverse temperature T_g/T for GeO_2, a system forming a network of strong intermolecular bonds, ortho-terphenyl, a weakly bonded molecular liquid, and glycerol, an 'intermediate' hydrogen-bonded liquid. For the former, the variation is almost linear (Arrhenius-like), whereas the two others are characterized, below some temperature T^*, by a strong departure from linear dependence (super-Arrhenius behaviour). (Data taken from references cited in reference [4].) (b) The effective activation free energy $E(T)$, obtained from data shown in (a), as a function of inverse temperature. Both $E(T)$ and T are scaled by the crossover temperature T^* shown in (a). ($T^* = 350$ K, 322 K, 1150 K for ortho-terphenyl, glycerol, and GeO_2, respectively.)

Lennard-Jones model behaves as a fragile liquid.) The plots are displayed in figure 2(a), where $E(T)$ is measured in units of $k_B T^*$, and in figure 2(b) where the deviation from the high-T Arrhenius value, $(E(T) - E_\infty)/k_B T^*$, is shown. The result is striking: the binary Lennard-Jones system appears as a strange hybrid. On one hand, it has very weak intermolecular bonding that leads to a small value of the high-T Arrhenius activation free energy $E_\infty/k_B T^* \simeq 2.45$ characterizing 'normal' liquid behaviour, in contrast to weakly bonded ortho-terphenyl for which the ratio is 9, to intermediate H-bonded glycerol for which the ratio is 18, and to the strong network-forming GeO_2 for which the ratio is 27; on the other hand, its departure from Arrhenius behaviour below T^*, when properly scaled to be compared to real glass-forming liquids as in figure 2(b), is comparable to that of the *strongest* glass formers, such as GeO_2, and is much less than that of fragile liquids like ortho-terphenyl†. We conclude that the binary

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† The relevant simulations were performed at *constant volume*, and the constant-pressure behaviour of the binary Lennard-Jones model has not been checked yet. It should be stressed, however, that a strong influence of density, resulting in a major difference between constant-pressure and constant-volume properties of the binary Lennard-Jones system, would be at odds with the behaviour of real supercooled liquids: see section 2.
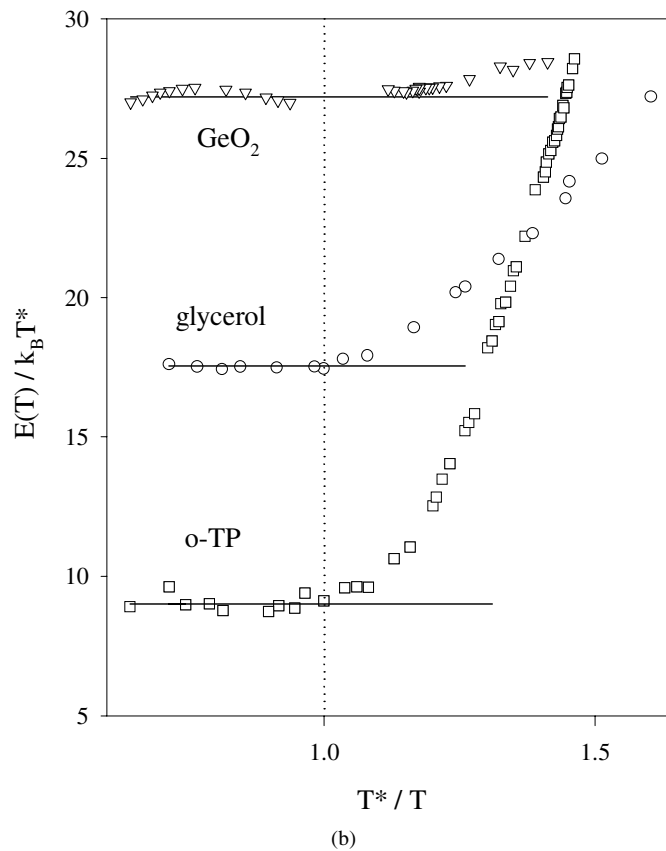
Figure 1. (Continued)

Lennard-Jones model appears to be a very weakly bonded, but nonfragile (in the sense of showing only weak super-Arrhenius behaviour) system. This conclusion, that contradicts the generally accepted view about the fragility of Lennard-Jones systems (including the recent suggestion, based on a rather indirect argument, by Angell et al [10] that the binary Lennard-Jones mixture is a moderately fragile liquid), stresses the importance of a proper scaling of the available data. In the case of Lennard-Jones models, the conventional use of T_g as a scaling temperature is questionable because the determination of T_g requires an uncontrolled extrapolation procedure, with molecular-dynamics simulation data stopping some ten or eleven orders of magnitude short of the typical α-relaxation time at the calorimetric T_g.

Other systems like one-component liquid models with atoms interacting through the Lennard-Jones and the Dzugutov [11] potentials are also very nonfragile. (Models of molecular liquids like ortho-terphenyl are not considered here.) Anticipating the analysis in the next section, we quantify the 'fragility' of a system by a parameter B that measures its degree of departure from Arrhenius behaviour (in a plot of $(E(T) - E_\infty)/k_B T^*$ versus T/T^*): the more fragile a system, the more super-Arrhenius the T-dependence of its viscosity and α-relaxation time, the larger B. For instance, the value of B is found to be more than 400 for the very fragile ortho-terphenyl whereas it is equal to 28 for the strong glass former GeO_2, and to 90 for the intermediate system glycerol [4]; in contrast we have found $B \simeq 1.0$, 1.3, and 5.4 for the one-component Lennard-Jones, the Dzugutov, and the binary Lennard-Jones systems,
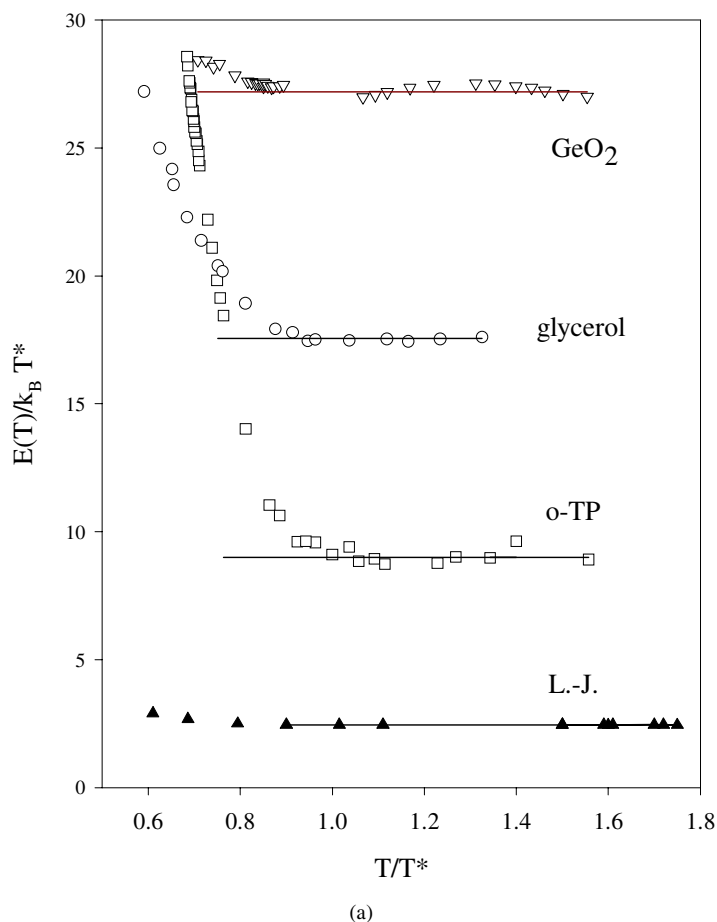
Figure 2. Relative 'fragility' (super-Arrhenius character) of the binary Lennard-Jones model compared to a strongly bonded, a weakly bonded, and an intermediate supercooled liquid. (a) The effective activation free energy $E(T)$ for GeO_2, glycerol, ortho-terphenyl, and the binary Lennard-Jones model, as a function of temperature. Both $E(T)$ and T are scaled by the crossover temperature T^*. Note that the data for $E(T)$ as well as the value of T^* for the binary Lennard-Jones model (at constant volume) are directly taken from reference [9]. (b) As (a), but with the high-T Arrhenius contribution subtracted for each system. The dotted lines represent the 8/3 power-law prediction of the frustration-limited domain theory, with the values of the (adjustable) parameter B taken from references [4] and [13] and given in the text.

respectively† [12, 13], values characteristic of very nonfragile liquids. The values obtained for B are somewhat dependent upon the fitting procedure, since the range of available relaxation times is much more limited for these computer studied systems than for real glass-forming liquids; however, the fact that the obtained values of B are typical of nonfragile liquids, with $B \leqslant 20$, seems robust.

† In the language of the frustration-limited domain approach (see section 4), B is inversely related to the strength of the inherent structural frustration in the system. The small values of B for the simple atomistic models composed of one or two species of spherical particles indicate that they are strongly frustrated. This can also be inferred from the work of Nelson and co-workers [14] on metallic glasses, where it was found that the density of defects associated with the frustration of icosahedral order is high, so correlation lengths never grow significantly beyond the interatomic distance.
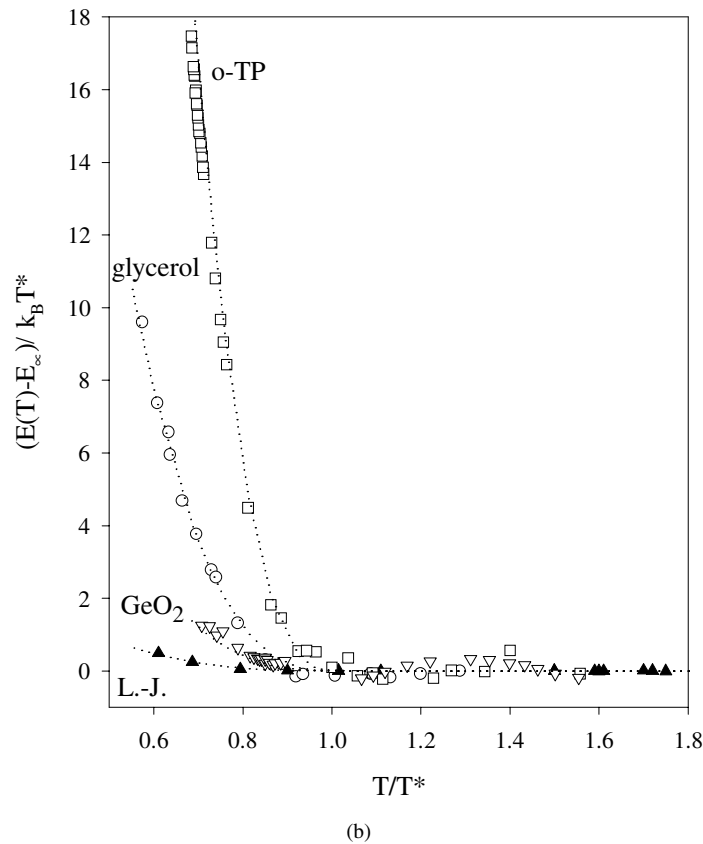
(b)

Figure 2. (Continued)

Supportive of the above conclusion are also the recent studies of one-component Lennard-Jones systems in which the slow relaxation is described kinetically by means of an appropriate master equation, acting in a potential energy landscape [15, 16]. Although finite-system-size effects, incomplete information on the connectivity between potential energy minima, and the use of other approximations in handling the master equation approach can still cast doubt on the validity and the generality of the results, one notices the remarkable finding of these studies, that the temperature dependence of the viscosity and relaxation time of Lennard-Jones systems is Arrhenius-like over the whole range of up to 13 decades in viscosity and time, a property suggestive of a nonfragile liquid! See figure 3(a) of reference [15] and figure 10 of reference [16]. The discussion above does not, of course, diminish interest in the study of relaxations in simple atomistic models per se; but it strongly questions the relevance of such studies in shedding light on the dominant mechanisms that lead to the glass transition of real fragile supercooled liquids.

4. Frustration-limited domain theory

The description of the viscous slowing down of weakly bonded glass-forming liquids as a super-Arrhenius activated process with sizable activation free energies is indicative of the presence of collective or cooperative phenomena; in addition, the heterogeneous nature of

the α-relaxation suggests that this collective or cooperative character shows up in supercooled liquids in the form of spatial domains, supermolecular regions over which dynamical properties are correlated. Numerous models have been based on the existence of domains, clusters, fluctuations, cooperative regions, and two-liquid phases [2]. While providing a reasonable way of fitting or rationalizing pieces of the phenomenology, these models usually leave unanswered the questions of why heterogeneities or domains appear in supercooled liquids and how they account for the activated nature of the α-relaxation. The theory of frustration-limited domains [17] addresses these basic questions. It is a nonmolecular, 'mesoscopic' approach, in which the driving force for domain formation and growth comes from an ordering transition that is aborted by the ubiquitous presence of structural frustration. We summarize this approach in what follows.

4.1. Physical picture

The basic physical ingredient is the concept of structural frustration. Molecules in a liquid, even in the 'normal' range above melting, tend to arrange themselves into a locally preferred structure corresponding to the minimization of an appropriate local free energy; but the spatial extension of this local arrangement is thwarted by ubiquitous structural frustration that prevents a periodic tiling of space by the locally preferred structure and is the source of a strain free energy that grows superextensively with system size. As a result of the competition between the short-range tendency to order, i.e., to extend the locally preferred structure, and the strain generated by frustration, the liquid, below some temperature T^*, breaks up into domains whose structure is the locally preferred, but strained, one associated with the high-T liquid, and whose size and further growth are limited by frustration. T^* is interpreted as marking a crossover between normal, molecular liquid behaviour ($T > T^*$) and collective, domain-influenced behaviour ($T < T^*$). As seen below, in the theory T^* does indeed mark the passage from Arrhenius-like to super-Arrhenius T-dependence of the α-relaxation time and viscosity that we have stressed in the preceding sections.

4.2. Theoretical model

The above picture can be incorporated in a coarse-grained model based on an effective Hamiltonian [17]. The locally preferred structure of the liquid is characterized by a local order variable $O(r)$ that can take a discrete set of orientations (more than 2), as in a clock model. The Hamiltonian consists of a reference term describing the short-range tendency to order and a weak, but long-range competing interaction that generates the frustration-induced strain:

$$H = -\sum_{r,r'} J(r - r')O(r) \cdot O(r') + \frac{Qa_0}{2} \sum_{r,r'} \frac{O(r) \cdot O(r')}{|r - r'|} \tag{2}$$

where $J(r)$ is a short-range 'ferromagnetic' interaction with a typical energy scale J, a_0 is the characteristic length associated with the local structure (of the order of the mean intermolecular distance in a liquid), and $0 < Q \ll J$. In the absence of frustration, the reference system undergoes a continuous ordering transition at a temperature $T^* \sim J$.

4.3. Avoided critical behaviour

Due to the long-range nature of the competing interaction that gives rise to a superextensive cost in free energy proportional to L^5, long-range order characteristic of the reference, unfrustrated system (here, ferromagnetic order) is completely prohibited by frustration, no matter how

small, but nonzero, this latter may be [17]. A still stronger statement can be made about the system's behaviour in the temperature–frustration (Q–J) phase diagram. An ordering transition, leading to a phase with modulated order (a 'defect-ordered phase'), can take place at a low temperature $T_{DO}(Q) < T^*$, but the critical point at (T^*, $Q = 0$) is *isolated*, i.e., no other critical points are present in its vicinity in the T–Q phase diagram. This property has been shown rigorously for the spherical version of the model [18] and for the O(n) version [19] with n strictly larger than two†, for which $\lim_{Q\to 0} T_{DO}(Q)$ is significantly less than T^*. For weak frustration, $Q \ll J$, the critical point at T^* is *narrowly avoided*, which results in the presence of two supermolecular lengths below T^*: the correlation length ξ_0 of the reference system, $\xi_0 \sim (T^*-T)^{-\nu}$ with $\nu \simeq 2/3$ for all standard three-dimensional critical systems in the absence of quenched disorder, and a new length, $L^* \sim (Q/J)^{-1/2}\xi_0^{-1} \sim (Q/J)^{-1/2}(T^* - T)^{+\nu}$, that is the characteristic scale over which the physics is essentially that of the unfrustrated system (which is ordered, since $T < T^*$) and that can be identified with the typical domain size [17].

4.4. Static and dynamic phenomenological scaling analysis

At temperatures sufficiently below T^*, such that $a_0 \ll \xi_0 \ll L^*$, one can develop scaling arguments to describe the collective contribution to both static and dynamic properties. The liquid is considered as a collection of (slightly) polydisperse, frustration-limited domains whose mesoscopic order parameters are randomly oriented. The static scaling analysis starts with the formulation of the free-energy density of a domain of size L in a random environment [17]:

$$\frac{F(L)}{L^3} = \frac{\sigma}{L} - \phi + sL^2 \tag{3}$$

where, as in a standard nucleation picture, the surface tension (σ) scales as ξ_0^{-2} and the ordering bulk free-energy density (ϕ) as ξ_0^{-3}; the additional term describes the frustration-induced strain, whose coefficient s is *a priori* unknown. Assuming that the *inter*domain interactions are sufficiently weak to be treated by a mean-field approach, one can derive the scaling form of the strain coefficient s by identifying the length that minimizes the free-energy density with the typical domain size L^*, namely $s \sim \sigma/(L^*)^3 \sim (Q/J)^{3/2}\xi_0$; this leads to the equilibrium distribution of domain sizes, $\rho(L, T)$, in a scaled form:

$$\rho(L, T) \propto \exp\left[-\gamma(T)\left(\kappa\left(\frac{L}{L^*}\right)^2 - \frac{3}{2}\left(\frac{L}{L^*}\right)^3 + \frac{1}{2}\left(\frac{L}{L^*}\right)^5\right)\right] \tag{4}$$

where the entire temperature dependence is contained in the parameter

$$\gamma(T) \sim (Q/J)(T^*/T)(1 - T/T^*)^{8/3}$$

and κ is a number of order 1.

The presence below T^* of internally ordered domains leads to slow, activated dynamics of the (discrete) order variable. By generalizing simple dynamic scaling arguments about slow relaxation in a finite-size system below its ordering transition via defect-wall creation, one can evaluate the collective (or cooperative) contribution to the activation free energy, $\Delta E(L, T)$, for a domain of size L; this latter takes the following scaled form [17]:

$$\frac{\Delta E(L, T)}{k_B T} = b\gamma(T)\left(\left(\frac{L}{L^*}\right)^2 - m\left(\frac{L}{L^*}\right)^5\right) \tag{5}$$

† For Ising spins ($n = 1$), the transition line to the defect-ordered phases goes continuously, albeit nonanalytically, to the critical point at T^* when $Q \to 0$. However, the transition in the presence of frustration is not continuous: it is driven *first-order* by the fluctuations [20].

where b and m are numbers of order 1, with $bm < 1/2$. The full effective activation free energy is then obtained by adding the molecular, Arrhenius-like contribution, $E_\infty/k_B T$, to the above expression. It is important to stress that the domains are equilibrium entities (in a supercooled liquid they are of course metastable relative to the crystal), and that the slow, activated dynamics does *not* correspond to out-of-equilibrium domain coarsening.

4.5. Main predictions

The central point of the theory concerns the prediction of a crossover from molecular, normal liquid behaviour to collective, domain-dominated behaviour around T^*, a crossover that explains the change from Arrhenius-like to super-Arrhenius T-dependence of the viscosity and α-relaxation time. The super-Arrhenius contribution to the activation free energy is described by a universal power law, i.e.,

$$E(T) = \begin{cases} E_\infty & \text{for } T > T^* \\ E_\infty + B(k_B T^*)\left(1 - \dfrac{T}{T^*}\right)^{8/3} & \text{for } T < T^* \end{cases} \quad (6)$$

which is a prediction that fits well the extant experimental data on glass-forming liquids. A central feature of the theory is that it predicts the nontrivial, and somewhat unusual, universal exponent 8/3, which has been reasonably well verified by experiment [4]. For an illustration, see figure 2(b) as well as references [4] and [17]. The parameter B in equation (6) is a measure of the departure from Arrhenius behaviour, and hence of 'fragility', and it is the one that we have used in the preceding section about the relevance of simple atomistic systems. From the scaling analysis, we obtain that $B \sim (Q/J)^{-1}$, so the more fragile (super-Arrhenius) a liquid, the less frustrated it is.

The dynamics is also naturally described as heterogeneous below the temperature T^* at which the liquid breaks up into supermolecular domains. For instance, the nonexponential character of the dielectric relaxation can be simply modelled by assuming that molecular reorientations are completed within a single domain, in which they are dynamically coupled to the order variable, and by assuming that the relaxation within each domain is exponential in time. This leads to the following expression for the (normalized) dielectric relaxation function [17]:

$$f_\alpha(t) = \int_0^\infty \mathrm{d}L \, L^2 \rho(L, T) \exp\left[-\frac{t}{\tau_{\alpha,\infty}} \exp\left(-\frac{E_\infty + \Delta E(L, T)}{k_B T}\right)\right] \quad (7)$$

for which $\rho(L, T)$ and $\Delta E(L, T)$ are given by the theory. As illustrated in figure 3, by comparing to the experimental data on the imaginary part of the frequency-dependent dielectric susceptibility of the fragile glass former salol [21], the above equation (or rather the Fourier transform of $\mathrm{d}f_\alpha(t)/\mathrm{d}t$), together with the scaling expressions for $\rho(L, T)$ and $\Delta E(L, T)$ given in equations (4) and (5), allow one to reproduce quite well the main features of the α-relaxation with a small set of temperature-independent parameters. More details will be given in a forthcoming publication.

The relevance of the frustration-limited domain theory to the description of other aspects of the phenomenology of supercooled liquids, such as the decoupling of translational and rotational relaxation, the avoidance of the Kauzmann entropic catastrophe, and the possible observation of 'defect-ordered phases' at low temperature, is discussed elsewhere [22].

4.6. Open questions

A fundamental theoretical uncertainty yet to be resolved is that of whether the assumptions that underlie the phenomenological scaling analysis leading to activated, heterogeneous dynamics

Salol Dielectric Data
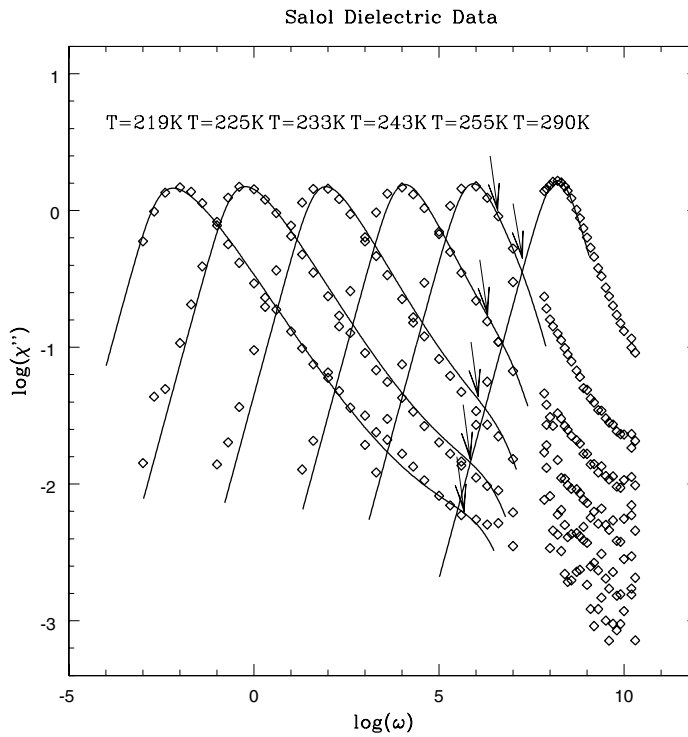
Figure 3. Comparison between the frequency-dependent dielectric susceptibility of the fragile glass former salol and the predictions of the frustration-limited domain theory, equations (4), (5), and (7); $\log_{10}(\chi''(\omega))$ is plotted versus $\log_{10}(\omega)$ at several temperatures. The temperature- and frequency-independent parameters κ, b, and m are obtained by fitting the data: $\kappa = 0.84$, $b = 1.46$, $m = 0.20$. The other parameters are taken from reference [4], and the experimental data are taken from reference [21]. Due to its nonmolecular, mesoscopic character, the theory has an intrinsic upper-frequency cut-off, $\omega_{cut} \sim (\omega_\infty/10) \exp(-E_\infty/k_B T)$, marked by the arrows.

evolve rigorously from the Hamiltonian in equation (2) (completed by some short-time dynamics for the spin variables). A more physical problem is that of mapping the local order and the frustration in a given liquid, however they are defined, onto the local order variable, $O(r)$, and onto the frustration parameter Q (or equivalently onto B).

5. Conclusions

In this article, we stress that the salient feature to be explained about the glass transition is the temperature-controlled super-Arrhenius activated nature of the viscous slowing down of supercooled liquids, more strikingly seen in weakly bonded, fragile systems. In the light of this observation, we have compared the behaviour of simple models involving one or two components of spherically interacting atoms with that of real glass-forming liquids and shown that, although being very weakly interacting systems, these simple models are at the same time nonfragile, in the sense that their viscosity and α-relaxation time show little departure from Arrhenius temperature dependence. Finally, we have summarized how our approach to supercooled liquids, based on frustration-limited domains, can explain the main aspects of the phenomenology, including the crossover from Arrhenius to super-Arrhenius behaviour and the heterogeneous character of the α-relaxation.

Acknowledgments

References

[1] Ediger M D, Angell C A and Nagel S R 1996 *J. Phys. Chem.* **100** 13 200
[2] Sillescu H 1999 *J. Non-Cryst. Solids* **243** 81
[3] Angell C A 1985 *Relaxation in Complex Systems* ed K L Ngai and G B Wright (Arlington, TX: Office of Naval Research) p 3
   Angell C A 1991 *J. Non-Cryst. Solids* **131–133** 13
[4] Kivelson D, Tarjus G, Zhao X-L and Kivelson S A 1996 *Phys. Rev.* E **53** 751
[5] Stickel F, Fisher E W and Richert R 1995 *J. Chem. Phys.* **102** 6251
   Stickel F, Fisher E W and Richert R 1996 *J. Chem. Phys.* **104** 2043
[6] Fisher D S, Grinstein G M and Khurana A 1988 *Phys. Today* **41** (Dec) 56
[7] Ferrer M L, Lawrence C, Demirjian B G, Kivelson D, Alba-Simionesco C and Tarjus G 1998 *J. Chem. Phys.* **109** 8010 and references therein
[8] Li G, King H E Jr, Oliver W F, Herbst C A and Cummins H Z 1995 *Phys. Rev. Lett.* **74** 2280
[9] Sastry S, Debenedetti P G and Stillinger F H 1998 *Nature* **393** 554
[10] Angell C A, Richards B E and Velikov V 1999 *J. Phys.: Condens. Matter* **11** A75
[11] Dzugutov M 1992 *Phys. Rev.* A **46** R2984
[12] Ferrer M L, Sakai H, Kivelson D and Alba-Simionesco C 1999 *J. Phys. Chem.* **103** 4191
[13] Tarjus G, Alba-Simionesco C, Ferrer M L, Sakai H and Kivelson D 1999 *Slow Dynamics in Complex Systems* ed M Tokuyama and I Oppenheim (Washington, DC: ACS Books) p 406
[14] Sachdev S and Nelson D R 1984 *Phys. Rev. Lett.* **53** 1947
   Sachdev S and Nelson D R 1985 *Phys. Rev.* B **32** 1480
   Nelson D R and Spaepen F 1989 *Solid State Physics* vol 42 (New York: Academic) p 1
[15] Angelani L, Parisi G, Ruocco G and Viliani G 1998 *Phys. Rev. Lett.* **81** 4648
[16] Miller M A, Doye J P K and Wales D J 1999 *Phys. Rev.* E **60** 3701
[17] Kivelson D, Kivelson S A, Zhao X-L, Nussinov Z and Tarjus G 1995 *Physica* A **219** 27
   Kivelson D and Tarjus G 1998 *Phil. Mag.* B **77** 245
[18] Chayes L, Emery V J, Kivelson S A, Nussinov Z and Tarjus G 1996 *Physica* A **225** 129
[19] Nussinov Z, Rudnick J, Kivelson S A and Chayes L 1999 *Phys. Rev. Lett.* **83** 472
[20] Viot P and Tarjus G 1998 *Europhys. Lett.* **44** 423
[21] Dixon P K, Wu L, Nagel S R, Williams B D and Carini J P 1990 *Phys. Rev. Lett.* **65** 1108
   Wu L, Dixon P K, Nagel S R, Williams B D and Carini J P 1991 *J. Non-Cryst. Solids* **131–133** 32
[22] Tarjus G and Kivelson D 1995 *J. Chem. Phys.* **103** 3071
   Kivelson D and Tarjus G 1998 *J. Chem. Phys.* **109** 5481
   Kivelson D, Pereda J-C, Luu K, Lee M, Sakai H, Ha A, Cohen I and Tarjus G 1997 *Supercooled Liquids: Advances and Novel Applications (ACS Symposium Series 676)* ed J Fourkas *et al* (Washington, DC: ACS Books) p 224