Dynamically Correlated Regions and Configurational Entropy in Supercooled Liquids

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When a liquid is cooled below its melting temperature, if crystallization is avoided, it forms a glass. This phenomenon, called *glass transition*, is characterized by a marked increase of viscosity, about 14 orders of magnitude, in a narrow temperature interval. The microscopic mechanism behind the glass transition is still poorly understood. However, recently, great advances have been made in the identification of *cooperative rearranging regions*, or *dynamical heterogeneities*, i.e., domains of the liquid whose relaxation is highly correlated. The growth of the size of these domains is now believed to be the driving mechanism for the increase of the viscosity. Recently a tool to quantify the size of these domains has been proposed. We apply this tool to a wide class of materials to investigate the correlation between the size of the heterogeneities and their configurational entropy, i.e., the number of states accessible to a correlated domain. We find that the relaxation time of a given system, apart from a material dependent prefactor, is a *universal function* of the configurational entropy of a correlated domain. As a consequence, we find that, at the glass transition temperature, the size of the domains and the configurational entropy per unit volume are anticorrelated, as originally predicted by the Adam−Gibbs theory. Finally, we use our data to extract some exponents defined in the framework of the *random first-order theory*, a recent quantitative theory of the glass transition.

1. Introduction

Following the seminal paper of Adam and Gibbs,[1] the concept of *cooperative rearranging regions* (CRRs) has become ubiquitous in the literature on the glass transition. In fact, the cooperative relaxation of such regions is proposed by many theories to be the elementary rearrangement mechanism taking place in the liquid close to the glass transition temperature T_g, and the increase of the size of these regions (or *dynamical correlation length* ξ) upon decreasing the temperature is proposed to be responsible for the dramatic slowing down of the dynamics around T_g.

Roughly speaking, the Adam−Gibbs (AG) theory proposes the existence of CRRs of size ξ, whose relaxation time $\tau(\xi)$ is given by

$$\tau(\xi) \sim \tau_0 \exp\left[\left(\frac{\xi}{\xi_0}\right)^d \frac{\Delta}{K_B T}\right] \tag{1}$$

i.e., it is activated with a barrier proportional to the number of units belonging to the CRR (here d is the space dimensionality, K_B is the Boltzmann constant, Δ and ξ_0 are system-dependent characteristic energy- and length-scale, respectively). Each CRR can be found in a certain number of internal states; this gives a "configurational entropy" contribution to the liquid entropy, and we indicate by $S_c(T)$ the configurational entropy per molecule. The total configurational entropy of a CRR (i.e., the logarithm of the number of states it can access) is called σ_{CRR}. It is a central quantity in the AG theory and turns out to be

$$\sigma_{CRR}(\xi) = \frac{S_c(T)}{K_B}\rho\xi^d \tag{2}$$

where ρ is the number density of molecules. For a region to be able to relax, the number of accessible states must be larger than a given threshold, let us say n_0. Therefore $\sigma_{CRR}(\xi) > \ln(n_0)$, which implies by eq 2 the existence of a lower cutoff $\tilde{\xi}$ on the size of the CRR given by $\tilde{\xi}^d \sim K_B \ln(n_0)/\rho S_c(T)$. Assuming that the dynamical decorrelation in the liquid is dominated by the shortest relaxation time (smaller CRR), and substituting the previous equation in eq 1, one is left with the celebrated AG relation:

$$\tau(T) \sim \tau_0 \exp\left(\frac{\Delta \ln(n_0)}{\rho\xi_0^d T S_c(T)}\right) = \tau_0 \exp\left(\frac{\mu}{T S_c(T)}\right) \tag{3}$$

As $S_c(T)$ is experimentally observed to be a decreasing function of temperature, and seems to vanish at the Kauzmann temperature T_K, both $\tilde{\xi}$ and $\tau(T)$ are predicted to grow and diverge at T_K by the AG theory. Note that, by construction, according to the AG theory, the "entropy" of the smallest CRR, which dominates the relaxation, is $K_B\sigma_{CRR}(T) = S_c(T)\rho\tilde{\xi}(T)^d \sim K_B \ln(n_o)$, i.e., it is a temperature-independent quantity.

The AG theory had an enormous impact, and relation 3 has been shown to be fairly well compatible with experimental data. Still, from the theoretical point of view, the AG scenario is not firmly established, mainly because of the unnatural scaling of τ with ξ in eq 1 (one would naturally expect an exponent $\psi < d$ related to the shape of the CRR−CRR interface).[2] Unfortunately, the size of CRRs cannot be estimated on the basis of

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TABLE 1: Summary of Data at T_g and References[a]

name	T_g	log τ_0	B	T_0	S_c	ΔC_p	β	m	$N_{corr,4}$	θ	ref. dyn.	ref. calor.
PC	155	−14.8	467	128	1.86	9.10	0.7	94	341	2.2	38, 39	40, 41
TNB	344	−18.0	1620	264	6.22	18.1	0.56	86	92	2.4	42, 43	13, 40, 44–47
OTP	244	−14.5	684	202	2.67	13.8	0.55	97	148	2.3	33, 36, 48, 49, [•]	36, 41, 50
PDE	294	−20.7	1793	215	4.22	13.2	0.73	84	207	2.4	49, 51, 52, [•]	[•]
DPVC	251	−19.0	1243	192	3.24	12.3	0.67	89	208	2.2	53, [•]	[•]
PPGE	258	−15.1	708	217	4.97	23.0	0.49	107	85	2.3	8, [•]	54
m-toluidine	185	−14.9	519	154	1.77	11.2	0.57	102	217	2.2	55, 56	57
PG	168	−12.9	708	120	2.28	8.06	0.72	53	129	2.1	58	59–62
GeO_2	816	−13.8	9732	199	1.08	0.75	1	21	413	2.4	63–65	37, 65
SiO_2	1452	−13.8	14562	530	0.65	0.37	0.7	25	579	2.5	63–65	63
$ZnCl_2$	385	−12.8	1647	274	0.63	1.89	0.71	51	499	2.2	66	60, 67
3-bromo-pentane	108	−12.9	374	83	2.81	9.09	0.62	64	124	2.3	36, 68	36
MTHF	90	−17.3	406	69	2.81	8.91	0.62	83	217	2.3	36, 68	36
n-propanol	100	−10.5	386	70	2.43	6.09	0.62	41	78	2.3	36, 68	36
salol	221	−15.9	823	175	3.46	13.2	0.58	86	135	2.3	36, 68	36
butyronitrile	95	−11.9	326	72	0.82	4.84	0.77	56	285	1.8	69	70
TPP	204	−17.5	704	169	4.18	18.2	0.51	111	125	2.3	41, 71	41
selenium	309	−15.5	1077	248	0.83	1.83	0.42	88	535	2.6	72, 73	60, 74
glycerol	188	−14.7	973	130	3.18	10.0	0.68	54	97	2.1	68, 75, 76	40, 41
toluene	116	−15.1	328	97	1.49	8.71	0.55	103	267	2.2	77, 78	41
B_2O_3	553	−10.7	2540	353	3.18	3.25	0.62	35	107	2.5	79, 80	31, 37, 47, 60, 61

[a] When more databases were present, we compared the data and verified the consistency. [•] indicates original data from this work. Most of the dynamic data come from dielectric relaxation experiments, except for GeO_2 and SiO_2 (viscosity was used instead of τ), for B_2O_3, $ZnCl_2$ (photon correlation spectroscopy), and selenium (mechanical relaxation). Temperatures are in K, times are in s, entropy and specific heat are in units of R. Note: PC = propylene carbonate, TNB = trinaphthyl-benzene, OTP = *O*-terphenyl, PDE = phenolphtaleindimethylether, DPVC = diphenyl-vinylidene carbonate, PPGE = polyphenylglycidylether, PG = propylene glycol, MTHF = 2-methyltetrahydrofuran, and TPP = triphenylphosphite.

the AG theory alone;[3,4] values of $\tilde{\xi}$ estimated on the basis of different improvements of the AG theory are not always consistent (see, e.g., refs 3–8) and no clear-cut evidence of a growth of $\tilde{\xi}$ could be obtained within this approach.

In the past decade, two major advances have been made in understanding the relaxation phenomena that are behind the AG picture. First, Kirkpatrick, Thirumalai, and Wolynes[9,10] identified a deep analogy between the behavior of supercooled liquids and that of a class of mean field spin glass models. These models are characterized by the existence of an exponentially large (in the system volume V) number N_s of metastable states at low temperature, that give a finite contribution $S_c(T) = K_B/\rho V \ln N_s$ to the liquid entropy, to be identified with the configurational entropy of AG. The mean field scenario was then used as a starting point for a nucleation theory of supercooled liquids, the *random first-order theory* (RFOT).[2,11–14] Second, a method to estimate the size of the CRR in experiments was proposed by Berthier at al.[15,16] We will now briefly review these results.

As in the AG theory, in the RFOT theory, the liquid close to T_g is supposed to be a "mosaic state" made of CRRs of typical radius ξ; one assumes that, inside a CRR, the system behaves almost as a mean field system. Then one can show[2] that, for a CRR in a state A, the free energy cost for nucleation of *any possible state* $B \neq A$ in a droplet of linear dimension r is

$$\Delta F_{AB}(r) = -TS_c(T)\rho r^d + \gamma r^\theta \quad (4)$$

The configurational entropy turns out to be the driving force for nucleation, while γ is a surface tension, which is assumed to be roughly constant around T_g and the exponent $\theta < d$. Note that the free energy barrier for a given state is given only by the surface term. The bulk term comes from the fact that the number of possible different states is exponentially large in the volume of the droplet, i.e., there is an entropic gain in changing state inside the droplet. The typical size $\tilde{\xi}$ of the CRR is given by the condition $\Delta F_{AB}(\tilde{\xi}) = 0$, because, for larger sizes, nucleation inside a CRR is not avoidable, and the CRR looses its identity.[2] This gives

$$\tilde{\xi} = \left(\frac{\gamma}{\rho T S_c}\right)^{\frac{1}{d-\theta}} \quad (5)$$

as an upper bound for the size of CRRs. As smaller sizes give a bigger ΔF (see eq 4), one can conclude that this is indeed the size that dominates the partition function.[2]

The *thermodynamic* free energy barrier for nucleation of a different state inside a CRR is the maximum of $\Delta F_{AB}(r)$, which is found in $\tilde{r} = (\theta/d)^{1/(d-\theta)}\tilde{\xi}$ and is given by

$$\Delta F_{AB}(\tilde{r}) \propto \rho \tilde{\xi}^d T S_c(T) = K_B T \sigma_{CRR}(T) \quad (6)$$

i.e., in the RFOT, the thermodynamic barrier for nucleation is given by the total configurational entropy of CRRs of typical size $\tilde{\xi}$. Note that in RFOT, using eqs 5 and 6, $\sigma_{CRR}(T) \sim S_c(T)^{-\theta/(d-\theta)}$ and is expected to diverge at T_K, while, in the AG theory, it is a constant by definition.

One of the most interesting open problems in RFOT is the relation between this thermodynamic barrier for nucleation of a droplet with the relaxation time of the system. Usually it is assumed that $\tau \sim \exp(\Delta F_{AB}(\tilde{r})/K_B T) \sim \exp[\sigma_{CRR}(T)]$, as proposed in refs 17, 13, and 14. More generally, one can expect that $\tau \sim \exp[\sigma_{CRR}(T)]^\psi$, and the exponents ψ and θ can be adjusted to recover the AG relation (eq 3) without imposing eq 1. While the exponent ψ is difficult to compute analytically, estimates of the exponent θ have been obtained by means of instantonic techniques.[18,19]

The main problem in RFOT is that the domain size $\tilde{\xi}$ is not directly observable; in fact, the quest for a growing length-scale in supercooled liquids was for a long time unsuccessful, as static correlation functions such as the structure factor do not reveal any sign of long-range order setting in upon approaching T_g. A major theoretical advance in this direction has been achieved in the past decade by identifying a family of dynamic[20–24] and static[2,25–27] many-points correlation functions, inspired by the mean field models, that define correlation lengths that are predicted to increase fast upon approaching T_g.

Still these correlations are not directly accessible in experiments; nevertheless, experimental evidence for a growing number of correlated units involved in the relaxation has up to now been obtained by different techniques (see ref 28 for a review).

Very recently, Berthier et al.[15,16] proposed a very general but still simple and direct method to measure a "number of correlated units" $N_{corr}(T)$ in glass-forming systems. They were able to relate, by a fluctuation–dissipation-like theorem, the four-point correlations introduced in refs 20–22 to an easily accessible response function, namely, the derivative of a dynamic two-point correlation (such as, for example, the intermediate scattering function) with respect to an external control parameter such as temperature or density. Their result can be formulated as follows:

$$N_{corr,4}(T) = \frac{K_B}{\Delta C_p(T)} T^2 \{\max_t \chi_T(t)\}^2 \qquad (7)$$

where $\chi_T(t) = dC(t)/dT$ is the temperature derivative of a suitable correlation function, and ΔC_p is the configurational heat capacity per molecule at constant pressure. In fact, eq 7 is a lower bound for $N_{corr,4}$, but one can show[15,16,23,24] that it gives a very good estimate of this quantity; all the details of the derivation can be found in ref 16. Moreover, one can simplify the analysis by assuming that $C(t)$ has a stretched exponential form, $C(t) = \exp(-(t/\tau_\alpha(T))^{\beta(T)})$. Then one has

$$N_{corr,4}(T) = \frac{K_B}{\Delta C_p(T)} \frac{\beta(T)^2}{e^2} \left(\frac{d \ln \tau_\alpha}{d \ln T}\right)^2 \qquad (8)$$

plus two corrections: one involving $d\beta(T)/dT$, the other coming from a shift of the maximum of χ_T that, for large stretching, is not found in $t = \tau_\alpha$. Both corrections can be shown to be irrelevant for the following analysis, giving an error on the order of 1% of the value of $N_{corr,4}$. Note also that the temperature dependence of the stretching parameter $\beta(T)$ is weak around T_g, especially when plotted against log (τ_α) (see, e.g., Figure 2c in ref 29). Experimental values of $N_{corr,4}$ were reported in refs 15 and 16 for some prototypical glass-forming systems, and it was shown that this quantity indeed increases upon approaching T_g.

The aim of this paper is to compute $N_{corr,4}$ for a large number of glass-forming materials and compare it to the configurational entropy. We *hypothesize that $N_{corr,4}$ is representative of the size of a CRR*, i.e., that $N_{corr,4} \sim \rho\xi^d$; this identification between dynamically correlated units and CRR is, in general, nontrivial, as it is possible to give examples where it does not hold.[16,23,24] Still, in the specific case of glass-forming liquids, it is at least partially supported by theoretical arguments.[2,16,23–27] It is worth noting that $N_{corr,4}$ is larger than the size of the CRRs estimated on the basis of the AG picture;[3–7] this might be due to the scaling postulated by AG, eq 1, which might be incorrect (see ref 2 for a more detailed discussion). Anyway, in ref 3, $N_{corr} \sim 35-290$ is reported, which is not very different from the values of $N_{corr,4}$ found here and in ref 16. In particular, in ref 8, the value $N_{corr} = 75 \pm 20$ is reported for polyphenylglycidylether (PPGE), in good agreement with our estimate of $N_{corr,4}$ for the same material, reported in Table 1.

Inspired by the AG and RFOT theories, following eq 2, we define the logarithm of available states in a correlation volume as

$$\sigma_{CRR}(T) = \frac{S_c}{K_B} N_{corr,4} = \frac{S_c}{\Delta C_p} \frac{\beta^2}{e^2} \left(\frac{d \ln \tau_\alpha}{d \ln T}\right)^2 \qquad (9)$$

As we discussed above, AG theory predicts σ_{CRR} to be independent of temperature, while RFOT predicts that it is an increasing function of temperature, and predicts relations between the relaxation time $\tau_\alpha(T)$ and $\sigma_{CRR}(T)$. The aim of this work is to test these predictions.

From the experimental point of view, there is an important advantage in working with σ_{CRR} instead of $N_{corr,4}$. In fact, in experiments, one usually deals with molecular liquids or polymers, where the constituents of the liquid are complex units, and it is not clear *a priori* what are the relevant degrees of freedom that are related to the glass transition. Thus, $N_{corr,4}$ and S_c have to be normalized to a "number of relevant degrees of freedom" (or *beads*) per unit volume. This is also needed if one wants to extract the precise value of ξ. A procedure to define these beads has been proposed by Stevenson and Wolynes;[30] the bead count provided by their formula is close to, but not identical with, that obtained using chemical knowledge of molecular flexibility, and thus depends on molecular substructure. On the contrary, σ_{CRR} represents the number of states accessible to a CRR and is independent of the number of relevant degrees of freedom inside this region. In fact, in eq 9, the dependence on the bead density is cancelled by taking the ratio $S_c/\Delta C_p$. Therefore our analysis does not require a precise determination of the bead density; note that, for that reason, we do not report precise numerical values of ξ.

2. Experimental Methods

For each analyzed material, we collected original and literature data for the relaxation time $\tau_\alpha(T)$, the stretching exponent $\beta(T)$, the configurational entropy $S_c(T)$ and heat capacity $\Delta C_p(T)$ as functions of temperature at constant pressure. From these quantities we compute $N_{corr,4}$ and σ_{CRR} according to eqs 8 and 9, following the procedures already detailed in ref 16. Some remarks on the data analysis are worth noting at this point:

1. S_c and ΔC_p are not directly accessible by experiments. Following an approximation commonly adopted in literature, we estimated these quantities from the excess entropy of the supercooled liquid with respect to the crystal (we used the fits reported in the literature or original data obtained for this work). This approximation gave rise to several criticisms: for instance, the difference of anharmonicity between the crystal and the supercooled liquid could reflect in a vibrational contribution to the excess entropy (see, e.g., ref 31). One should also consider the contribution of the secondary processes, when present.[32] All these discrepancies could induce an overestimation of S_c up to 50%. Nevertheless, as the excess entropy is believed to often be proportional to S_c, we used it as an estimation, as previously done in the literature.

2. The determination of the stretching parameter is also a possible source of error. Sometimes it has been done in the literature by fitting the whole correlation function and subtracting the contribution of additional fast processes. These procedures are often model dependent, and can induce an error of up to 10% in the value of β. Indeed, in some papers, the β of dielectric structural relaxation has been underestimated by using a fitting procedure on a log–log scale, which emphasized the high frequency tail of the loss peak. For these cases, β has been estimated here by using a fitting procedure mainly sensitive to the region of the full width at half-maximum.

3. We fitted literature data for $\tau_\alpha(T)$ by a Vogel–Fulcher–Tamman (VFT) law, $\tau_\alpha(T) = \tau_0 e^{[B/(T-T_0)]}$, in a temperature range

TABLE 2: Data at T_g and References for the Molecular Liquids Used in Figure 3

name	T_g	S_c	ΔC_p	β	m	$N_{corr,4}$	ref. dyn.	ref. calor.
sorbitol	268	4.41	28.8	0.48	128	94	68, 81	37
ethylbenzene	115	2.82	9.67	0.68	58	115	37	82
isopropyl benzene	126	2.52	10.2	0.56	90	179	56, 68	37, 41
triphenylethene	248	5.46	14.5	0.5	91	102	37, 83	31, 37
ethylene glycol	153	2.04	7.58	0.78	52	156	37, 84	31, 37
ethanol	97	1.63	5.46	0.7	55	195	37	31, 37
3-methylpentane	77	3.07	8.66	0.62	56	100	37, 68	31, 37
diethyl phthalate	180	3.03	15.3	0.64	78	117	85	31
a-phenyl-cresol	220	3.34	15.4	0.53	83	90	68, 86	86
glucose	309	2.97	17.3	0.37	115	74	37, 87, 88	37, 60, 61, 89
indometacin	318	4.55	19.8	0.59	75	71	37, 90	37

Same units as in Table 1.

TABLE 3: Data at T_g and References for the Polymeric Liquids Used in Figure 3

name	T_g	S_c	ΔC_p	β	m	$N_{corr,4}$	ref. dyn.	ref. calor.
PVC	354	0.28	2.33	0.27	191	818	68,91	32,91
PET	342	1.08	9.36	0.48	156	430	68,91	32,91
a-PMMA	378	0.58	3.61	0.37	145	572	68,91	32,91
PS	373	0.60	3.40	0.35	143	528	68,91	32,91
PP	270	0.63	2.44	0.37	137	755	68,91	32,91
PDMS	146	0.42	3.07	0.56	100	734	68,91	32,91
PIsop	200	0.80	3.71	0.47	77	251	68,91	32,91
PPO	195	1.13	3.86	0.52	74	275	68,91	91
PIB	200	3.56	2.56	0.55	46	179	68,91	91
PE	237	0.67	1.26	0.55	46	364	68,91	32,91
PEN	390	0.85	10.1	0.48	140	320	32,68	37
PEEK	419	0.54	10.4	0.32	280	554	32,68	32
Pcarb	420	1.22	7.21	0.35	132	212	32,68	32

Same units as in Table 1. For some systems reported by ref 32, a particular procedure, introduced there, was used to subtract from the excess entropy the contribution of the secondary relaxation.

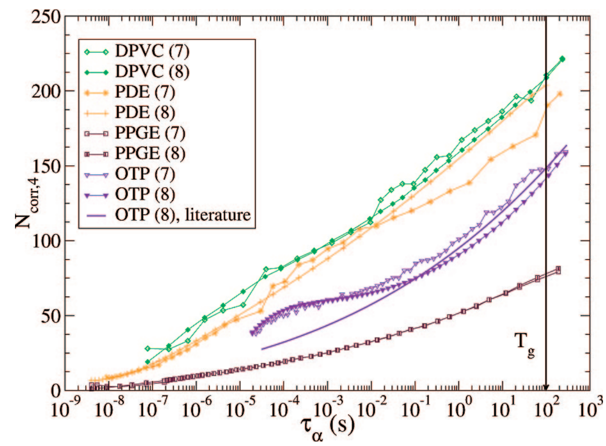

Figure 1. Original data for $N_{corr,4}$, computed by (*i*) direct measurement of the dielectric spectra using eq 7, and (*ii*) fitting the measured $\tau_\alpha(T)$ and using eq 8, for four different materials. In the case of OTP, we compare our data with the estimate of $N_{corr,4}$ obtained from the VFT fit reported in ref 36. A discrepancy is observed at small times, while, in the interesting region of large relaxation times, all the results are consistent.

around T_g, where reliable data are available. The VFT parameters are reported in Table 1. For most of the systems, we found, as already observed in the literature,[33,36] that only one VFT law was not able to fit the data in the whole temperature range, and that only in a region close to T_g was the AG relation satisfied: in these cases, only data belonging to this region were reported. In some cases we did not have access to the raw data but only to the VFT fit reported in the literature. Note that the characteristic time τ_0 obtained from the VFT fit is not the $T \to \infty$ limit of $\tau_\alpha(T)$, as the fit is performed in an interval close to T_g where data are available. This is consistent since we are interested in the "effective" physical attempt frequency close to T_g. The derivative d ln τ_α/d ln T was obtained from the VFT fit when it is reliable (see ref 33 for details). In the cases where VFT gave a poor fit, we directly derived the data (if dense enough) or we used a polynomial interpolation.

4. We do not report here a systematic analysis of experimental errors; correspondingly, error bars are not reported in the figures. Errors are, generically, on the order of 10% of all quantities, mainly coming from the difficulty in the determination of β and S_c as discussed above. For some materials, different data sets were available: we checked that the analysis using different sources gives consistent results within these errors. In Tables 1, 2, and 3 we report the list of the investigated materials and the sources of the data.

To check the robustness of our results, we measured the dielectric permittivity $\varepsilon(\omega)$, related to the dipole–dipole correlation, of four different substances: OTP (see also ref 16), DPVC, and PPGE, obtained from Sigma-Aldrich, and PDE that was kindly provided by Dr. Marian Paluch, University of Katowice, Poland. Frequency was spanned in the range of 0.1 mHz to 3 GHz using a combination of Novocontrol Alpha Analyzer (up to 10 MHz) and Agilent Network Analyzer (up to 3 GHz). Experimental methods used for this experiment are similar to others already performed in the past and already discussed in detail in refs 34 and 35.

A fine temperature scan gives direct access to the temperature derivative $\chi_T(\omega) = \mathrm{d}\varepsilon(\omega)/\mathrm{d}T$, from which we can determine $N_{corr,4}$ by using eq 7, where time is replaced by frequency. The procedure we followed and the results are identical to the ones reported in Section III of ref 16. In Figure 1 we report the values of $N_{corr,4}$ for these four substances determined by using eqs 7 and 8: the close agreement between the two estimates is a check of the validity of the approximations discussed above. Then, for the rest of our analysis, we will use eq 8 to estimate $N_{corr,4}$.

3. Results

In Figure 2, left panel, we report the parametric plot of $N_{corr,4}(T)$ versus $\tau_\alpha(T)$ for the 21 materials listed in Table 1. Our results closely agree with the ones already reported in refs 15 and 16: we observe an increase of $N_{corr,4}$ upon lowering the temperature, consistently with the prediction of a growing cooperativity in supercooled liquids. Note that we added to the plot some materials that were not analyzed in ref 16; this is because the liquids studied in ref 16 all have similar values of $S_c(T_g)$ and of VFT parameters, which then give similar values of $N_{corr,4}$ around T_g (see Table 1). We added to the plot materials like selenium, TPP, and TNB, whose configurational entropy

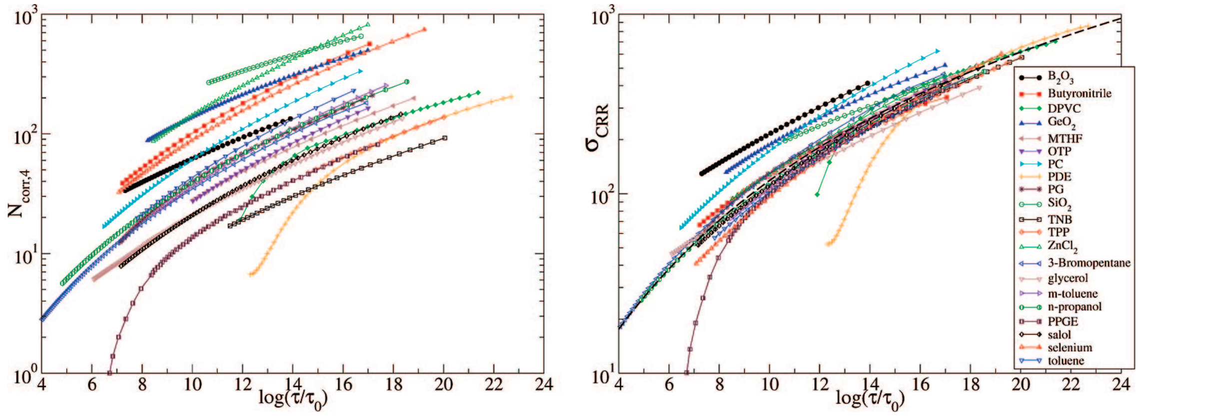

Figure 2. (Left) $N_{corr,4}$ as a function of $\log(\tau_\alpha/\tau_0)$ and (right) σ_{CRR} as a function of $\log(\tau_\alpha/\tau_0)$ for the materials listed in Table 1. In the right panel, the spreading of the curves is, at fixed $\log(\tau_\alpha/\tau_0)$, about a factor of 2, while in the left panel it is about a factor of 20. The dashed line is $\log(\tau_\alpha/\tau_0) = (\sigma/\sigma_0)^\psi + z \ln(\sigma/\sigma_0) + \ln A$, with $A = 0.65$, $\sigma_0 = 2.86$, $z = 1.075$, and $\psi = 0.5$.

at T_g is very different from the one of glycerol and other molecular glass formers. For this reason, the spreading of data in our figure is more marked than in ref 16, about a decade at fixed $\log(\tau_\alpha/\tau_0)$. Some of these systems are expected to severely test any kind of correlation between thermodynamic and dynamic properties, as they are also known as "bad actors" concerning the link between kinetic and themodynamic fragility.[37]

In the right panel of Figure 2 we show that the data collapse much better on a universal curve when σ_{CRR} is plotted instead of $N_{corr,4}$. This result suggests that $\tau_\alpha(T)$ is given by a material-dependent characteristic attempt rate τ_0 times a *universal function* of the thermodynamic barrier $\sigma_{CRR}(T)$, i.e.,

$$\log[\tau_\alpha(T)/\tau_0] = F[\sigma_{CRR}(T)] \tag{10}$$

with $F[\sigma]$ being an almost universal function.

To give more robustness to this result, one would like to add much more materials to the plot. Unfortunately, for most materials calorimetric data and/or the stretching exponent are reported only at T_g, and the previous analysis is not possible. We thus resort to a weaker test: for most materials $\tau_0 \sim 10^{-15}$ s, therefore the glass transition temperature T_g is roughly defined by $\log[\tau_\alpha(T_g)/\tau_0] = 17$. If eq 10 holds, we expect

$$\sigma_{CRR}(T_g) = \frac{S_c(T_g)}{K_B} N_{corr,4}(T_g) \sim F^{-1}[17] \tag{11}$$

which implies an inverse correlation between S_c and $N_{corr,4}$ at T_g. These quantities can be easily computed from the values of $S_c(T_g)$, $\Delta C_p(T_g)$, $\beta(T_g)$, and fragility $m = (\mathrm{d} \log \tau_\alpha/\mathrm{d} \log T)|_{T=T_g}$, that are reported in the literature for many more materials (see Tables 2 and 3 for their list and the references). We can then test the prediction (11) on a larger set of 45 materials. In Figure 3 we plot $N_{corr,4}(T_g)$ as a function of $S_c(T_g)$; the plot is compatible with an inverse correlation of these two quantities.

Note that from eqs 11 and 8 it follows easily that $S_c(T_g)\beta^2 m^2/\Delta C_p(T_g)$ = const. Using the well-known relation $m/17 \sim \Delta C_p(T_g)/S_c(T_g)$, which follows from the AG relation (eq 3), we obtain $\beta^2 m$ = const. The latter relation has already been derived in refs 13 and 14 in a different way and seems to be well verified in real materials, which is a nice consistency check of our results.

3.1. Exponents. Having stated our main experimental results (eqs 10 and 11), we can turn to a more detailed comparison with RFOT. First we note that the experimentally observed increase of $\sigma_{CRR}(T)$ on lowering the temperature is not compatible with AG theory, while it fits well into the RFOT scenario.

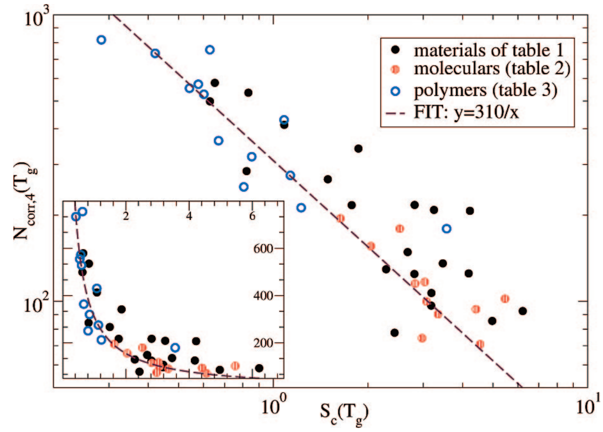

Figure 3. Plot of $N_{corr,4}(T_g)$ as a function of $S_c(T_g)$ (in units of R) for the 45 materials listed in Tables 1, 2, and 3. The dashed line is a fit to the inverse correlation predicted by eq 11. In the inset, the same plot is reported in linear scale.

Then we would like to extract the values of the RFOT exponents from the experimental data: we anticipate that this is a very difficult task given the large experimental errors already discussed and the probable importance of preasymptotic effects. Still we observe that, identifying $N_{corr,4} \propto \rho\tilde{\xi}^d$ and using eqs 5 and 6, RFOT predicts the relation

$$\sigma_{CRR}(T) \sim S_c(T)^{-\theta/(d-\theta)} \sim \tilde{\xi}^\theta \sim N_{corr,4}^{\theta/d} \tag{12}$$

In Figure 4 we plot $N_{corr,4}$ as a function of σ_{CRR} for the materials of Table 1. The power-law relation predicted by RFOT is very well verified, and the resulting values for the exponent θ are in the range 2.2–2.5 (see Table 1). Note that RFOT usually assumes $\theta = 1.5$,[13,14] while istantonic calculations[18,19] give $\theta = 2$ (see Figure 4). This result is then quite puzzling; note, however, that the relation $N_{corr,4} \sim \tilde{\xi}^d$ is not well established,[16] and this could affect the result for θ.

We can also try to estimate the exponent ψ that relates the relaxation time to σ_{CRR}, $\tau_\alpha \sim \tau_0 \exp(\sigma_{CRR}^\psi)$. To account for preasymptotic effects, we choose a specific form[16] $F[\sigma] = (\sigma/\sigma_0)^\psi + z \ln(\sigma/\sigma_0) + \ln A$ in eq 10 to fit the curves in the right panel of Figure 2. We obtain as a best fit a value of $\psi \sim$ 0.4–0.5; note, however, that, by changing the other parameters, one can obtain quite good fits for a range of values of ψ = 0.3–1.5.

From $\log(\tau_\alpha/\tau_0) \sim \sigma_{CRR}^\psi$ and eq 12 one obtains

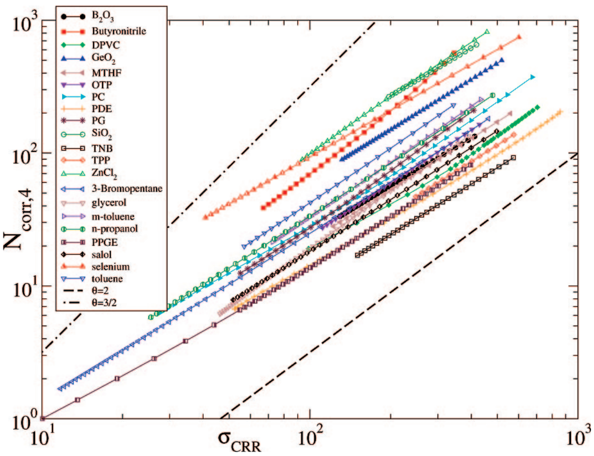

Figure 4. Parametric plot of $N_{\mathrm{corr},4}(T)$ as a function of $\sigma_{\mathrm{CRR}}(T)$ for the materials in Table 1. The dashed line corresponds to the istanton result $\theta = 2$, and the dot−dashed line corresponds to the RFOT conjecture $\theta = 3/2$.

$$\log \frac{\tau_\alpha(T)}{\tau_0} \propto S_c(T)^{-\theta\psi/(d-\theta)} \qquad (13)$$

which is consistent with the AG relation (eq 3) only if $\theta\psi/(d - \theta) = 1$. Assuming this and $\psi \sim 0.4-0.5$, we get $\theta \sim 2-2.15$, which is consistent with the values reported in Table 1. The coincidence of these two estimates of θ might support the robustness of the indication that its value should be close to or slightly larger than 2.

The result for $\psi \sim 0.4-0.5$ is less reliable. Still, we obtain a strong indication that $\psi < 1$, which implies that the relaxation time diverges *slower* than the exponential of the thermodynamic barrier. This suggests the existence of relaxation paths that are more efficient than simple nucleation of a random state inside a CRRs. A theoretical description of such processes is still lacking.

Conclusions

We collected original and literature data on a set of 45 glass-forming materials and, exploiting the methods of refs 15 and 16, we show that (*i*) the size of the CRRs, which we estimate by $N_{\mathrm{corr},4}$, is inversely correlated with the configurational entropy per unit volume at $T = T_g$ (eq 11) and (*ii*) more generally that the relaxation time seems to be a universal function of the configurational entropy of a CRR (eq 10), in a wide range of temperatures around T_g. We compared these results with theoretical predictions and found good agreement with the RFOT scenario. We also gave an estimate of the exponents θ and ψ of RFOT and found unexpected but still reasonable values of these exponents.

We wish to stress again that, in our analysis, we made the strong hypothesis that $N_{corr,4}$, as defined in ref 16, is representative of the size of a CRR, i.e., that $N_{\mathrm{corr},4} \propto \rho\xi^d$. A different scaling would not only change our estimates for the RFOT exponents, but change the definition of σ_{CRR} and ultimately destroy the scaling of the curves in the right panel of Figure 2. The consistency of our results seem to support the validity of this assumption; see, however, refs 23, 24, and 16 for a more detailed discussion.

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