PHYSICAL REVIEW E **97**, 032116 (2018)

Cooperativity in plastic crystals

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(Received 13 December 2017; revised manuscript received 9 February 2018; published 16 March 2018)

A statistical mechanical model previously adopted for the analysis of the α-relaxation in structural glass formers is rederived within a general theoretical framework originally developed for systems approaching the ideal glassy state. The interplay between nonexponentiality and cooperativity is reconsidered in the light of energy landscape concepts. The method is used to estimate the cooperativity in orientationally disordered crystals, either from the analysis of literature data on linear dielectric response or from the enthalpy relaxation function obtained by temperature-modulated calorimetry. Knowledge of the specific heat step due to the freezing of the configurational or conformational modes at the glass transition is needed in order to properly account for the extent to which the relaxing system deviates from equilibrium during the rearrangement processes. A number of plastic crystals have been analyzed, and relatively higher cooperativities are found in the presence of hydrogen bonding interaction.

DOI: 10.1103/PhysRevE.97.032116

I. INTRODUCTION

Orientationally disordered (or plastic) crystals (ODICs) consist of molecules which, although regularly arranged in a lattice, still maintain the ability to change their mutual orientations in a more or less constrained fashion. The relaxation dynamics associated to these degrees of freedom shares two main features with the α-relaxation observed in ordinary supercooled liquids, namely, a relatively broad and asymmetric frequency profile, and a super-Arrhenian temperature dependence of the central relaxation time. On cooling, the orientational motions progressively slow down until, at a certain temperature T_g, a process similar to a structural glass transition takes place and an orientational glass forms.

These circumstances make ODICs particularly interesting in the perspective of an understanding of the glass transition phenomenon. Brownian-like diffusion, for example, is absent in these systems, and the observed "glassy" dynamics involves only part of the whole ensemble of the degrees of freedom. Issues like the nature of the super-Arrhenian behavior, which in structural glasses is customarily associated to cooperative diffusional motion, within regions that progressively enlarge on cooling [1] must be reconsidered from a different and more general point of view.

The problem of the characteristic length associated to the structural glass transition and, more generally, the problem of estimating the cooperativity N_α (the average number of units participating in a rearrangement) as a function of temperature came about also in relation to the hypothesis that the large apparent activation energy of the α-relaxation near T_g would depend on N_α itself [2]. This association finds its roots in the idea that large energies should accompany the simultaneous displacement or activation of large numbers of units. When treating the orientational dynamics in plastic crystals, the concept of cooperativity may still be a reference, but of course in a generalized form.

Concerning instead the origin of the dynamical heterogeneity, the eventuality that relatively low cooperativities can be found even close to T_g [cf., e.g., Ref. [3] for adamantanes; see also the discussion in Refs. [4,5] with reference to levoglucosan (LG)] put forward the question whether the observed nonexponentiality in the orientational relaxation might not be necessarily associated to large characteristic relaxation lengths, but rather that it is intrinsic in nature. This is not a trivial issue, considering also that there is experimental evidence pointing in this direction (cf., e.g., Ref. [6]).

The above arguments highlight the importance of estimating the cooperativity in glass formers in general, whatever the mechanisms through which it shows up. In this scenario, a multiple-point correlation function approach [7,8] was adopted for the description of the α-relaxation, with the aim of extracting the cooperativity length in a system (at a certain temperature) from its *linear* response [9]. Later a related method was developed [10,11], based on the analysis of the *nonlinear* response. Its application to structural as well as to orientational glass formers can be found, e.g., in Refs. [1] and [12], respectively.

Recently, an independent method for estimating the cooperativity has been presented [13,14]. In this approach, N_α is worked out from an analysis of the relaxation function, based on the idea that in any cooperative rearrangement the spontaneous regression of a local, pretransitional dynamic state formerly established by fluctuations is inherent. A thermodynamic potential is associated to this pretransitional state, while cooperativity is in fact introduced by imposing that the deviation from thermodynamic equilibrium is stationary. The presence of constraints to the configurational or conformational motion is expressed in terms of (fluctuating) energy barriers, without specific reference to their nature. With this construction, reasonable estimates of the cooperativity in structural glass formers, close to T_g, were worked out

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2470-0045/2018/97(3)/032116(9)

on the basis of relaxation measurements (e.g., calorimetric, mechanical, or dielectric) carried out in the *linear* regime. Knowledge of the configurational entropy as a function of temperature also made possible improving the reliability of the estimates above T_g.

In this paper we provide a new derivation of the model, which is then used for the analysis of cooperative relaxation in ODICs.

II. THEORY

The present section is devoted to a brief qualitative illustration of a semiphenomenological model originally developed for the α-relaxation in supercooled liquids (cf. Refs. [13,14] for further details). In order to better address the point, we proceed from a known theoretical scheme proposed to describe systems close to the ideal glass transition [15].

Consider a glass former in contact with a heat bath, and let Γ be its configurational phase space. On cooling, the representative point of the system tends to dwell ever longer within subregions $\Gamma_k \subset \Gamma$ of relatively limited extension (hereafter called "components" as in Ref. [15]). These regions are mutually disjointed and such that

$$\Gamma = \bigcup_k [\Gamma_k \cup \partial\Gamma_k], \tag{1}$$

where $\partial\Gamma_k$ is a boundary region surrounding Γ_k. Within each of them, thermal equilibrium is reached rapidly, the associated free energy being given by $F_k \equiv F[\Gamma_k] = -k_B T \ln Z_k$, with Z_k the appropriate local partition function and $k_B T$ the thermal energy. Migration to another component $\Gamma_{k'}$ is possible provided a suitable fluctuation

$$\Delta F_k \equiv F[\partial\Gamma_k] - F[\Gamma_k] \tag{2}$$

takes place.

Reference [15] focuses in particular on the case in which confinement into any component whatsoever lasts much longer than the observation time. This situation has been later considered for the treatment of liquids close to the ideal glassy state [16]. In such conditions the free energy $F[\Gamma]$, which would characterize the system should it be capable of exploring the whole phase space, cannot be representative of an actual physical state. On the other hand, if p_k stands for the probability that the system resides in Γ_k, one can define an average free energy

$$\overline{F} \equiv \sum_k p_k F_k; \tag{3}$$

its significance involves issues like the appropriate p_k-distribution to choose or the influence thermal history has on it. One assumes that

$$\overline{F} = F[\Gamma] - k_B T \sum_k p_k \ln p_k. \tag{4}$$

Indeed, this relation follows wherever the distribution $p_k \equiv Z_k / \sum_k Z_k$ can be adopted, since neglecting contributions to Z_k from states at the boundaries, one has $F[\Gamma] \simeq -k_B T \ln(\sum_k Z_k)$; on the other hand, in the case that p_k is not known, Eq. (4) would properly describe, e.g., a condition of maximum missing information [15].

The logarithmic contribution in Eq. (4) is extensive provided the number of components grows exponentially with the size of the system. This problem has to do with the dependence of the number of inherent structures (i.e., the number of minima in Γ of the global potential energy Φ) on the number of units of which the whole system is made. The exponential form follows if it is assumed that there always exists a minimal volume wherein units can be relocated without significantly affecting the surroundings [17]; this is a basic concept characterizing also our idea of cooperativity.

Here we consider the case in which transitions among different components are possible within the observation time scale, so that $F[\Gamma]$ does have a physical counterpart.

In a stationary state, each free energy F_k associated to the corresponding Γ_k may be conveniently expressed as a sum of a "bulk" term $F_{b,k}$ plus a contribution ΔF_k related to the crossing of boundaries. The distribution p_k extremizes the expression

$$F[\Gamma] = \sum_k p_k \{F_{b,k} + \Delta F_k + k_B T \ln p_k\} \tag{5}$$

under the constraint that the average chemical potential remains constant (cf. also Ref. [15]); this is the basis of our approach to the analysis of the α-process.

Since any component may be probed by the system during the observation time, all bulk terms must be equal, i.e., $F_{b,k} \equiv F_b \; \forall k$; their contributions to the whole free energy is thus irrelevant for the determination of p_k because the normalization condition $\sum_k p_k = 1$ holds. On the other hand, the remainder of Eq. (5) comes into play when the rearrangement barriers are being crossed and is central to finding p_k through a proper analysis of the α-process. That is indeed the way through which the cooperativity N_α has been eventually estimated in Refs. [13,14] [cf. Eq. (14) below and the preceding Eqs. (7) and (13)]. Of course, this procedure implicitly selects a subset of components within which transitions from one Γ_k to another are observable through degrees of freedom relevant to the α-process (not mentioning the further limitations inherent to the experimental technique that is used in practice).

In considering ordinary (polymeric) liquids, configurational transitions have been treated as regressions of energy fluctuations. Rearrangements of a few units take place first, as a manifestation of a pretransitional dynamic state characterized by *nondiffusional* motion (*small-scale* rearrangements); then, under the conditions expressed by Eq. (9) below, *large-scale* diffusional motion may follow by facilitation, contributing to (part of) the configurational entropy.

This picture is consistent with the idea that, in supercooled liquids, motion is mainly nondiffusional with infrequent large length jumps [18,19].

In the pretransitional state the system explores phase space regions of relatively limited extension, given the nondiffusional character of the motion and the expected limits in the peak values of the momenta; the units involved in these configurational transitions are not more than the typical number filling a minimal volume of those mentioned above. As large-scale diffusional motion sets in, the representative point of the system has the possibility to reach regions of the phase space which are located at some distance from those just left; this is the way the system *tends* to equilibrium.

The treatment is now restricted to the case in which the free energy of Eq. (5) refers to one of these minimal volumes, i.e., in fact to what can be called a cooperatively rearranging region (CRR). The pretransitional state (which was referred to as the "interfacial dynamic state" in Ref. [14]) will represent the main focus in the following, since it amply suffices as a basis for the discussion of the results; facilitation, instead, whose rough description in Ref. [14] needs be improved, will be duly considered in future work.

We proceed by splitting the *excess* chemical potential associated to the nondiffusional dynamic regime as $\mu_k \equiv \mu_0 + \Delta\mu_k$. The first term (which must not be confused with a bulk contribution) is common to all components' boundaries and may carry a temperature dependence; it accounts for possible intermediate processes necessary for the attainment of the pretransitional state. For example, the weakening of hydrogen bindings (where present) before a local rearrangement dynamics sets in would contribute to μ_0. Once the intermediate μ_0-state has been reached, the subsequent redistribution among different Γ_k's takes place as a thermalization process. (In past accounts of the theory μ_0 was not considered, since applications to polymeric liquids did not suggest this term could be relevant [13]; on the other hand, approximate analyses on low molecular weight systems have been carried out in such a way that a finite μ_0 could be overlooked [14,20].)

In this way we are led to find the minimum of the configurational part of $F[\Gamma] - F_b$, under the condition that $\overline{\Delta\mu} \equiv \sum_k p_k \Delta\mu_k = \text{const}$. More explicitly, switching to a single-unit description, the extremum of the function

$$A \equiv U - TS + \lambda\overline{\Delta\mu} + \mu_0 \tag{6}$$

has to be found, where λ is the Lagrange multiplier associated to the constraint on $\overline{\Delta\mu}$, while S is the entropy introduced by the logarithmic term of Eq. (5). The energy involved in the boundary crossings consists of a fluctuating part U, which together with S and $\overline{\Delta\mu}$ is a functional of p_k, and a possible steady contribution encompassed in μ_0.

Inspired by the work of Adam and Gibbs [2], who mainly focused on energy fluctuations for the treatment of cooperative rearrangements, we chose to partition the phase space in components which differ from one another by the height of the energy barrier that needs be overcome to cross their own boundaries. If ζ stands for the barrier height referred to a single unit, then $S \equiv -k_B \sum_\zeta p(\zeta) \ln p(\zeta)$ is the entropy in the new representation; its meaning is now associated to the random change of ζ accompanying each configurational or conformational transition [21].

Denote by w_ζ the probability that a unit, formerly trapped in a well of depth ζ, reaches mobility after gaining energy enough to overcome the barrier; then its excess chemical potential is $\Delta\mu(\zeta) = -k_BT \ln w_\zeta$, and the extremization of A yields

$$p(\zeta) = Z_p^{-1}\, e^{-[w_\zeta\langle E\rangle_\zeta + \lambda\Delta\mu(\zeta)]/k_BT}, \tag{7}$$

where $Z_p \equiv \sum_\zeta \exp[-(w\langle E\rangle + \lambda\Delta\mu)/k_BT]$ normalizes p; $\langle E\rangle_\zeta$ is the weighted mean of the single-unit energies above ζ, and $w_\zeta\langle E\rangle_\zeta$ is its further average over long times [indeed, $\sum_\zeta p\, w_\zeta\langle E\rangle_\zeta$ gives U in Eq. (6)].

In Eq. (7) $\exp[-\lambda\Delta\mu(\zeta)/k_BT] = w_\zeta^\lambda$, that is, a unit may reach the state of mobility provided λ further units interacting with it do the same; in other words, the "specific cooperativity" λ relates with the condition that $\overline{\Delta\mu}$ must be a constant.

The probability p of Eq. (7) reflects, by its intrinsic nature, the random wandering of a mobile unit among different "trap states," each characterized by its own ζ-value. This is further clarified by the form of the potential

$$-k_BT \ln Z_p = \overline{w\langle E\rangle + \lambda\Delta\mu} - TS, \tag{8}$$

which can be immediately obtained by substituting Eq. (7) in the expression of the entropy. Equation (8) points out the role of "missing energy" played by the term containing the specific cooperativity λ (i.e., that $\lambda\Delta\mu$ adds to $w\langle E\rangle$ to give $\langle E\rangle$); equivalently, one may notice this directly from the argument of the exponential in Eq. (7). This is more than a formal adscription and leads to an important relation to be derived shortly [Eq. (11) below].

The deviation from equilibrium at temperatures below T_g can be related to the lack of specific configurational entropy, s_c, through the relation $s_c = (\overline{\Delta\mu} + \mu_0)/T$ (cf. Sec. 20 in Ref. [22], and in particular Fig. 3). An out-of-equilibrium condition persists also around T_g, and above this temperature as long as the activated character of the configurational motion dominates. The triggering of a facilitation process is an attempt to recover this equilibrium and the condition for its occurrence, starting from a pretransitional state with chemical potential $\Delta\mu(\zeta) + \mu_0$, is that

$$\Delta\mu(\zeta) + \mu_0 \geqslant T\, s_c. \tag{9}$$

Equation (9) is to say that the probability $\exp[-(Ts_c - \mu_0)/k_BT]$, associated to a state of diffusional motion, must be larger than the probability $\exp[-\Delta\mu/k_BT]$ of a nondiffusional dynamic state with *excess* energies $E > \zeta$.

We now focus on the average of the barrier values, ζ^*, for which Eq. (9) is fulfilled, that is, we limit our interest to the fluctuations which may eventually be observed in a relaxation experiment. Close to T_g, one has $\langle E\rangle_\zeta \simeq \zeta^*$, and the adscription mentioned above, referred to the densities around ζ^* in Eq. (8), leads to

$$\lambda\Delta\mu^* \equiv (1 - w^*)\zeta^* \tag{10}$$

(where the asterisk denotes any function of ζ whatsoever, evaluated at $\zeta = \zeta^*$), that is, using Eq. (9):

$$\lambda \approx \frac{\zeta^*}{T\, s_c - \mu_0}. \tag{11}$$

Equations (10) and (11) say that a finite specific cooperativity is intrinsically connected with the existence of a rearrangement barrier ζ^*; the second one, in particular, stresses a bit more the fact that this connection inheres an out-of-equilibrium state.

Although referring to just *one* mobile unit, the entropy S increases linearly with λ. This sort of extensivity is peculiar: it connects the multiplicity of well depths randomly probed by a single mobile unit whatsoever (cf. S), to the number λ of other units which are dynamically correlated with it; Eq. (11) eventually links this multiplicity to the rearranging energy barrier ζ^*. In the end, recalling note [21], a relationship between number of potential energy wells and the rearrangement barrier is recovered.

In order to apply the above construction to the analysis of relaxation, a suitable form has to be given to w_ζ. The assumption that the pretransitional motion is nondiffusive in character is introduced in our model by associating a unit the

TABLE I. Measurement and glass transition temperatures, T and T_g, respectively (both in K), specific heat step ΔC_p (approximate) at T_g in units of k_B, fitting parameters [n, λ, z, $\tau^* \equiv 1/\nu^*$ (in s) and μ_0 (in kJ/mol)], and relevant outcomes for the thermodynamic variables [$\overline{\Delta\mu}$, $\Delta\mu(\zeta^*,n)$ and ζ^*, all in kJ/mol] for the systems considered: Levoglucosan (LG), cyclo-hexanol (Cy-Hex), cyclo-octanol (Cy-Oct), cyano-adamantane (Cn-Adm), iso-cyano-cyclo-hexane (i-Cn-Cy-He), and propylene carbonate (PCA). The source of relaxation data is indicated by the index following the acronym of each system; references from which the Vogel temperature T_0 and ΔC_p are extracted are also indicated. The specific configurational entropy times the temperature, Ts_c (in kJ/mol), is explicitly reported for easy checks of both the difference $Ts_c - \mu_0$ associated to the large-scale rearranging motion, and its ratio with ζ^* (which relates to Eq. 11). The cooperativity N_α [Eq. (14)] is reported in last column. Except in the case of LG, for all other systems the analysis has been performed on dielectric relaxation data.

System	T [K]	ΔC_p [k_B]	T_0 [K]	T_g [K]	n	λ	z	τ^* [s]	$t_{\min}$ [s]	ζ^* [$\frac{\text{kJ}}{\text{mol}}$]	$\overline{\Delta\mu}$ [$\frac{\text{kJ}}{\text{mol}}$]	$\Delta\mu(\zeta^*,n)$ [$\frac{\text{kJ}}{\text{mol}}$]	μ_0 [$\frac{\text{kJ}}{\text{mol}}$]	Ts_c [$\frac{\text{kJ}}{\text{mol}}$]	N_α
LG	250	13.2	204.7[28]	247.8[4]	45	48.3	5	0.06	0.3	95	1.05	1.53	4.31	5.37	250
Cy − Hex[34]	150	3.9[35]	110[34]	151[34]	23	31.6	3.1	4.8	20	31.5	1.09	1.29	0.83	1.48	101
„	154				21	23.3	3.2	0.1	2	31.4	1.5	1.7	0.63	1.64	78
„	160				18	16.7	3.7	10^{-3}	0.02	30	1.84	2.19	0.44	1.9	66
Cy − Oct[12]	168	5[36]	73.6[36]	151[36][a]	25	32.7	1.6	24	40	37.8	1.07	1.35	4.91	5.65	54
„	172				25	31.7	1.7	3.8	6	38.7	1.12	1.4	5.15	5.93	55
„	178				23	27.4	1.5	0.43	0.6	37.5	1.22	1.55	5.48	6.34	43
„	182				24	28.5	1.5	0.1	0.2	39.7	1.2	1.54	5.8	6.7	45
Cn − Adm[37]	173	3.2[38]	70.3[38]	170[38]	11	5.9	1.5	0.03	0.1	27.5	3.08	4.97	0	4.12	10
„	183				10	6.5	1	0.01	0.02	25.5	2.68	4.85	0	4.61	8
i − Cn − Cy − He[39]	134	3.2[40]	84.66[39]	129[38]	8	8.9	1	1.2	2	13.7	1.58	2.28	0.2	1.63	10
„	145				7	7.3	1	0.005	0.01	14	1.74	2.72	0.25	2.06	8
PCA[41]	163	9.09[42]	134[41]	159[41]	40	62.7	2	0.02	0.04	54.7	0.78	0.95	1.92	2.36	130
	173				21	24.7	1.2	2×10^{-5}	3×10^{-5}	34	1.27	1.63	2.29	3.26	30
	183				13	11.9	0.9	2×10^{-7}	3×10^{-7}	26.2	1.83	2.63	2.3	4.19	11

[a].The dielectric glass transition is $T_g|_{\text{diel}} \approx 169$ K [12].

partition function proper of a *collection* of oscillators [23]. Thus we set $w_\zeta \equiv Z_\zeta / Z_0$, with

$$Z_\zeta \equiv Z_{\zeta,n} = \sum_{\zeta}^{\infty} \epsilon^n \, e^{-\epsilon/k_B T}, \tag{12}$$

being the exponent n appropriate for $n+1$ oscillators. By adopting this form, a dynamic coupling with (and among) the λ units of Eq. (11) is implicitly considered too. This is easily grasped by analogy with the harmonic approximation in the vibrational motion of polyatomic molecules, which gives rise to a number of normal modes ($n+1$ in the present case) for suitably defined collective coordinates. Implementation of Eq. (12) in data analysis always yields $\lambda \sim O(n)$, as can be seen, e.g., in Table I ($\lambda/n \sim 1$ would point to one-dimensional dynamic correlations).

At this stage, all the ingredients for estimating the cooperativity from relaxation data have been introduced. All we have to do is fit the relaxation function obtained experimentally (e.g., by mechanical, dielectric, or calorimetric spectroscopies) with the expression

$$\phi(t) \sim \int_0^\infty d\zeta \; p(\zeta) \exp\{-t \, \nu^* e^{-z\,\Delta\mu(\zeta)/k_B T}\}, \tag{13}$$

where t is the time, ν^* is a characteristic attempt rate, and z is the average number of units initiating the configurational transition (i.e., those rearranging at the small scale); the values of λ and z thus obtained yield the cooperativity through the expression

$$N_\alpha \approx z(\lambda + 1). \tag{14}$$

(It is worth recalling that the number of units participating in a pretransitional state is approximately the same as that involved in the subsequent large-scale rearrangement which follows facilitation [14].)

The general arguments outlined above have been initially applied to structural glass formers; in that case it is evident what diffusive or nondiffusive motion means. In the case of ODICs, the same concepts would be borrowed for the rotational degrees of freedom; thus, in a pretransitional state a unit's director would explore a limited portion of the solid angle, whereas the whole of it would be traced after facilitation has occurred.

III. EXPERIMENTAL

Levoglucosan or 1,6-anhydro-β-glucose ($C_6H_{10}O_5$, molar mass 162.14 g/mol) was purchased as crystalline powder of 99% purity from Aldrich Chemicals and kept in dry conditions until use. This precaution is necessary because the sample absorbs moisture from air, and the presence of moisture was found to promote transformation to the orientationally ordered crystal phase on cooling its ODIC phase and on heating its orientational glass.

Calorimetric measurements were performed using a Perkin-Elmer differential scanning calorimeter DSC 8500 equipped with an Intracooler III as a refrigerating system. The instrument was calibrated in temperature at a zero heating rate and in energy with high purity standards (indium, naphthalene, and cyclohexane), according to the procedure for standard DSC [24]. The sample, of about 20 mg, was contained in an aluminum DSC pan. Dry nitrogen was used as purge gas at a rate of 30 ml/min.

For preparing the ODIC phase the as-received sample was first heated up to 463 K at a rate of 20 K/min and kept at that temperature for 1 min to complete the transition to the liquid phase; then the sample was immediately cooled down to 273 K at −20 K/min.

To obtain accurate specific heat DSC data, $C_{p,\text{DSC}}$, measurements were done during repeated cycles between the temperatures of 273 K and 233 K at the scanning rates of ±20 K/min. The same procedure was adopted for the empty pans under identical conditions; the sample pan mass was known within a ±0.02 mg error.

The analyses by temperature-modulated differential scanning calorimetry (TMDSC) were done using a sawtooth modulation temperature program. The temperature modulated measurements were performed between 258 K and 238 K with a peak-to-peak temperature amplitude of 1.0 K, a modulation period of 60 s, and an underlying cooling rate of 0.1 K/min. The determination of the *complex* heat capacity $C_p \equiv C_p' - iC_p''$, and in particular the correction to the measured phase angle, was performed as described in Ref. [25]. The calibration factor of the complex heat capacity modulus was chosen so that the C_p' values below and above the glass transition matched with the corresponding $C_{p,\text{DSC}}$ values measured before.

IV. RESULTS AND DISCUSSION

The calorimetric data are processed like in Ref. [14]. An approximate enthalpy relaxation function, $\phi_H(t)$, can be obtained from the complex heat capacity C_p by means of the general fluctuation-dissipation relation [26]

$$C_p(\omega,T) = -\frac{1}{k_B T^2}\int_0^{+\infty} dt\, e^{-i\omega t}\,\frac{\partial \phi_H(t,T)}{\partial t} \tag{15}$$

and then associated to the peak temperature of the imaginary part C_p''. This derivation rests on the assumption that the time-temperature superposition applies, i.e., that $\phi_H(t,T) \equiv \phi_H(t/\tau)$, with $\tau(T)$ a characteristic relaxation time through which the temperature dependence is conveyed in ϕ_H; this implies that the integral in Eq. (15) is a function of just the product $\omega\tau$. The normalized heat capacity $C_{p,\text{norm}} \equiv [C_p - C_{p,\text{glass}}]/[C_{p,\text{liq}} - C_{p,\text{glass}}]$, where $C_{p,\text{liq}}$ and $C_{p,\text{glass}}$ are, respectively, the relaxed and unrelaxed contributions to C_p' extrapolated at the peak temperature (cf. Fig. 1), fulfils a relation similar to Eq. (15) where the prefactor $1/k_BT^2$ is absent and the relaxation function is normalized so that $\phi_{H,\text{norm}}(0) = 1$. We then chose for $C_{p,\text{norm}}$ an Havriliak-Negami (HN) representation:

$$C_{p,\text{norm}} = \frac{1}{[1 + (i\omega\tau_{\text{HN}})^a]^b}, \tag{16}$$

with a and b the width and asymmetry shape parameters, respectively (both lying in the interval]0,1]) and τ_{HN} is the temperature-dependent central relaxation time.

The upper panel of Fig. 1 shows the real and imaginary parts of the heat capacity; the asymmetry of the loss peak can be perceived by comparison with a Gaussian fit (short-dashed line).

The corresponding normalized Cole-Cole plot is reported in the lower panel of the figure (part of the data points have been skipped for clarity). Unlike the case of isothermal, scanning frequency measurements, here we have a fixed modulation frequency, while τ_{HN} varies with T. Since $C_{p,\text{norm}}'(\omega\tau_{\text{HN}})$ is invertible, we can construct the composite function $C_{p,\text{norm}}'' \equiv C_{p,\text{norm}}''(C_{p,\text{norm}}'; a,b)$, which, upon fitting the data (solid line), yields $a = 0.8 \pm 0.04$ and $b = 0.63 \pm 0.06$ as optimal shape parameters (after Ref. [27]; these values would approximately correspond to a stretching exponent $\beta \simeq 0.57$ in a Kohlrausch-Williams-Watts relaxation function). The T-dependence of the central relaxation time, obtained from the inverse function $\omega\tau_{\text{HN}} \equiv \omega\tau_{\text{HN}}(C_{p,\text{norm}}')$ and the temperature dependence of $C_{p,\text{norm}}'$ found experimentally, is shown in the inset "a" by open squares. Probably also due to the relatively high T-range of the analysis, $\ln[\tau_{\text{HN}}(T)]$ appears to be close to Arrhenian, with an activation energy $E_a \simeq 400$ kJ/mol (solid line). This is only apparently in disagreement with the behavior observed by recent dielectric spectroscopy measurements [28], which indicate for the ODIC

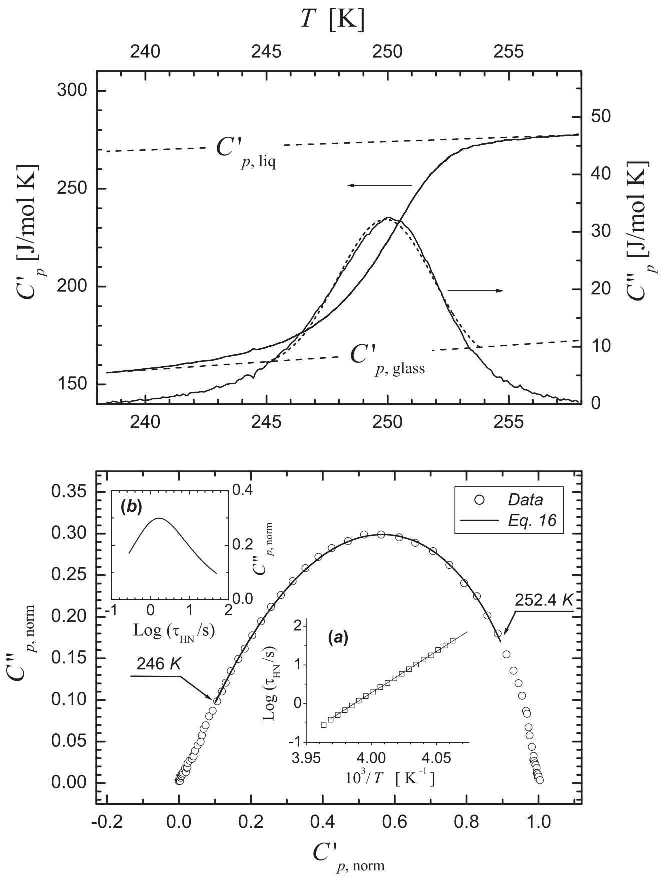

FIG. 1. Real and imaginary parts of C_p for LG (upper panel) obtained for a cooling rate of 0.1 K/min and a modulation frequency of $0.017\,\text{s}^{-1}$. The short-dashed line is a Gaussian fitting on C_p'' for the calculation of the cooperativity via Eq. (21); the straight dashed lines, $C_{p,\text{liq}}'$ and $C_{p,\text{glass}}'$ are the relaxed and unrelaxed contributions to C_p', respectively, extrapolated to the whole temperature interval displayed. The Havriliak-Negami expression of Eq. (16) (solid line) is adjusted to the corresponding Cole-Cole plot of $C_{p,\text{norm}}$ (lower panel) in the highlighted temperature interval. Inset "a" reports the T dependence of the central relaxation time (open squares) and the best fitting linear regression (solid line); inset "b" shows how the different modes contribute to $C_{p,\text{norm}}''$ depending on their characteristic relaxation time.

phase a Vogel-Fulcher-Tammann dependence

$$\tau_{\mathrm{HN}} = \tau_\infty \, e^{B/(T-T_0)} \tag{17}$$

with $\tau_\infty = 1.1 \times 10^{-13}$ s, $B \simeq 1376$ K, and $T_0 = 204.7$ K as fitting parameters; an *apparent* activation energy of about 350 kJ/mol is found indeed at $T = 250$ K from Eq. (17) (cf. also Ref. [4] for an independent analysis). We wish to point out that, despite its empirical nature, Eq. (16) reproduces the data very well in the interval of the analysis, the only assumption being that the time-temperature superposition holds.

The normalized enthalpy relaxation function is derived by inversion of Eq. (15), i.e., from the Fourier cosine transform of $C''_{p,\mathrm{norm}}$ as expressed by Eq. (16) with the HN shape parameters set at their best fit values, this time considering ω as integration variable and τ_{HN} fixed at its C''_p-peak temperature:

$$\phi_{H,\mathrm{norm}}(t) = \frac{2}{\pi}\int_0^\infty C''_{p,\mathrm{norm}} \cos(\omega t)\frac{d\omega}{\omega}. \tag{18}$$

Isothermal measurements in an appropriate range of frequencies would be preferable, where possible, like in the case of dielectric spectroscopy. In that case, the assumption of time-temperature superposition would not be that central for the derivation of ϕ from the data. We note that the HN analysis of the dielectric loss at $T \simeq 255$ K [cf. the inset of Fig. 3(a) in Ref. [28]] provides comparable results: $a = 0.77$ and $b = 0.51$.

Inset “b” of Fig. 1 shows how the different relaxation modes contribute to the loss peak, depending on their own relaxation time; clearly, the glass transition regime could not be closely approached, given the available modulation setting of the calorimeter.

The analysis of the relaxation function is done by adjusting Eq. (13) on $\phi_{H,\mathrm{norm}}(t)$; in our experience a fitting interval for which $0.7 \gtrsim \phi_{H,\mathrm{norm}} \gtrsim 0.07$ can be suggested. However, among the best fitting results one has to chose that for which the quantity

$$\mathbf{Sq} \equiv \left[1 - \frac{\zeta^*}{\lambda(T\, s_c - \mu_0)}\right]^2 + \left[1 - \frac{\Delta\mu(\zeta^*) + \mu_0}{T\, s_c}\right]^2 \tag{19}$$

is minimal, that is, a solution characterized by the minimum “distance” from both the conditions of Eqs. (9) and (11) set as equalities. Since μ_0 is not known in advance, one has to carry out a nested minimization procedure, that is, for initial μ_0 and n [cf. Eq. (12)] one fits $\phi_{H,\mathrm{norm}}$ and finds temporary values of λ, ζ^*, and $\Delta\mu(\zeta^*)$ [these latter via $Z_{\zeta,n}$ and Eq. (9)]; once **Sq** is computed, μ_0 and n are varied in order to minimize it.

The specific configurational entropy has been taken as

$$s_c = \Delta C_p \ln\left(\frac{T}{T_0}\right), \tag{20}$$

where ΔC_p is the specific heat step at T_g [which we set equal to $C_{p,\mathrm{liq}} - C_{p,\mathrm{glass}}$ at the peak temperature of $C''_p(T)$, that is, $\Delta C_p/k_B \simeq 13.2$ from the data of Fig. 1] and T_0 is the Vogel temperature of Eq. (17).

The results of the analysis are shown in Table I. Note that the cooperativity is rather high ($N_\alpha \simeq 250$), while $\mu_0 \simeq 4.31$ kJ/mol; thus, a significant fraction of the configurational entropy ($T s_c = 5.37$ kJ/mol) relates to the attainment of the pretransitional state, and only a small part of it has to be associated to the large-scale diffusional motion which eventually establishes at the end of the facilitation process; the latter initiates with rearrangements of just $z = 5$ molecules on average.

Of course, this result has to be considered an *estimate* of the cooperativity. There exist other independent methods for the evaluation of this or related quantities; given the difficulties in measuring “directly” the number of correlated units, this circumstance is particularly favorable because the result obtained by one method whatsoever can be taken as a reference for the others. For this reason we also derive below the LG cooperativity through Donth’s approach [29,30] and discuss, from our point of view, about the number $N_{\mathrm{corr},T}$ of units whose relaxation dynamics is correlated with a local enthalpy fluctuation [9,31].

According to Donth’s approach, we calculate the cooperativity through the formula

$$N_\alpha = \frac{k_B T^2}{\overline{\delta T^2}}\,\Delta\left(\frac{1}{C_p}\right), \tag{21}$$

where $\Delta(1/C_p) = 1/C_{p,\mathrm{glass}} - 1/C_{p,\mathrm{liq}}$ at the C''_p-peak temperature and $\overline{\delta T^2}$ is the mean square of the temperature fluctuations accompanying the energy exchanges among degrees of freedom *within* a CRR. From the data of Fig. 1, the amplitude of these temperature fluctuations can be estimated in $\delta T \simeq 2$ K by fitting $C''_p(T)$ with a Gaussian [32,33] (cf. the short-dashed line in the upper panel of Fig. 1); we then obtain $N_\alpha \sim 300$. Note that the same approach has been implemented in Ref. [28], yielding the rather smaller value of $N_\alpha \simeq 60$ at $T = 250$ K.

The most direct relation of Eq. (21) with our theory, is through the expression of the temperature fluctuations. In Ref. [13], indeed, it was shown that $\delta T \approx T(\Delta\mu^* - \overline{\Delta\mu})/\zeta^*$. From the data of Table I one finds $\delta T \simeq 1.3$ K, which, given the unavoidable error propagation, can be considered an acceptable approximation; however, it would not be convenient to use this value in Eq. (21) to derive N_α.

A further independent approach to the problem of cooperativity is through the dynamic susceptibility functions. In particular we focus on $\chi_T^{NVT}(t) \equiv (\rho/k_B T^2)\int d^3r\, \langle \delta e(\mathbf{0};0)\delta\phi(\mathbf{r};0,t)\rangle_{NVT}$, with ρ the number density, which describes how an energy fluctuation δe, occurring initially ($t = 0$) at a certain point $\mathbf{0}$, affects the relaxation dynamics, $\delta\phi$, a distance $\mathbf{r}$ apart. This three-point correlation is sensitive to what is considered to be a primary cooperativity mechanism [9] and is directly accessible experimentally because it is connected to the ordinary two-point relaxation function ϕ by the fluctuation-dissipation relation $\chi_T^{NVT} = \partial\phi/\partial T$. Assuming an energy fluctuation $\delta e \approx \sqrt{\Delta C_p k_B T^2}$, the number of units whose dynamics is affected by it is in the order of [9,31]

$$N_{\mathrm{corr},T} \sim \sqrt{\frac{k_B T^2}{\Delta C_p}}\max_t\left\{\left|\chi_T^{NVT}\right|\right\}. \tag{22}$$

The maximum is reached for t close to the central relaxation time τ of the process. (For the relationship of $N_{\mathrm{corr},T}$ with the nonlinear dielectric susceptibility, cf. Refs. [10,11].)

If the relaxation function is expressed with a stretched exponential $\exp\{-(t/\tau)^\beta\}$ and Eq. (17) is used for τ, then

$\chi_T^{NVT}|_{t\sim\tau} = (\beta/e)B\,T/(T-T_0)^2$ at its maximum. Hence, inserting the above values for LG, Eq. (22) would give $N_{\mathrm{corr},T} \sim 10$.

Once the relaxation data have been fitted, estimating $N_{\mathrm{corr},T}$ through Eq. (22) by means of our function would not yield a very different result. The point, however, is that the existence of a pretransitional state underlies the energy threshold expansion of Eq. (13); thus, in the present context, the reference state should be the excited one.

The role of primary dynamic correlation number is naturally played here by λ; in the cases where $\mu_0 \approx 0$, its relation with $N_{\mathrm{corr},T}$ follows from Eq. (22). Indeed, approximating the distribution in Eq. (13) as $p \sim e^{-\zeta/k_BT}$ [cf. Eq. (10)], one finds $\partial\phi/\partial T|_{t\sim\tau} \sim \zeta^*/k_BT^2$ [the contribution $\propto \partial\tau/\partial T$, being $O(z/\lambda)$, is neglected]; this implies $N_{\mathrm{corr},T} \approx \lambda\, s_c/\sqrt{\Delta C_p k_B}$. In cyano-adamantane, for example, the results listed in Table I yield $N_{\mathrm{corr},T} \sim 9$ at the temperature at which $\lambda \sim 6$ (note that $N_{\mathrm{corr},T} \simeq N_\alpha$ in this case, conforming to the class of non-Newtonian systems envisaged in Ref. [31]). However, when $\mu_0 \neq 0$ like in LG, the definition of $N_{\mathrm{corr},T}$ in the present framework may be not so obvious, in particular with regards to the appropriate energy δe to adopt as a reference.

A different context would characterize the *formation* of a pretransitional state, but this issue cannot be dealt with presently.

Turning now to the main track, Table I also shows the results of similar analyses carried out from the isothermal dielectric response of other ODICs [43], namely, cyclo-hexanol (Cy-Hex), cyclo-octanol (Cy-Oct), cyano-adamantane (Cn-Adm), and iso-cyano-cyclo-hexane (i-Cn-Cy-He). Although not able to form an ODIC, propylene carbonate (PCA) has been analyzed as well to help comparing with the results from nonlinear dielectric response [12]. More specifically, at about 183 K the ratio of PCA and Cy-Oct cooperativities found here seems to match rather well that obtained from the nonlinear analysis [the value 45/11, as from Table I, would be reasonably close to the ratio that can be extrapolated from the data of Fig. 4(b) in Ref. [12]]. On the other hand, we find a somewhat large cooperativity in PCA at 163 K (in Ref. [12] it would be as low as $N_\alpha \approx 35$, assuming $N_\alpha = 11$ at 183 K; this value seems too small, given the proximity to T_g).

Excluding LG, the results of Table I are reported in Fig. 2 for better clarity. From this figure it is evident how larger the cooperativities are in Cy-Oct and Cy-Hex compared to Cn-Adm and i-Cn-Cy-He; note, in addition, that the last two ODICs show quite the same cooperativities (approximated to the closest integer) in similar conditions with respect to their own T_g.

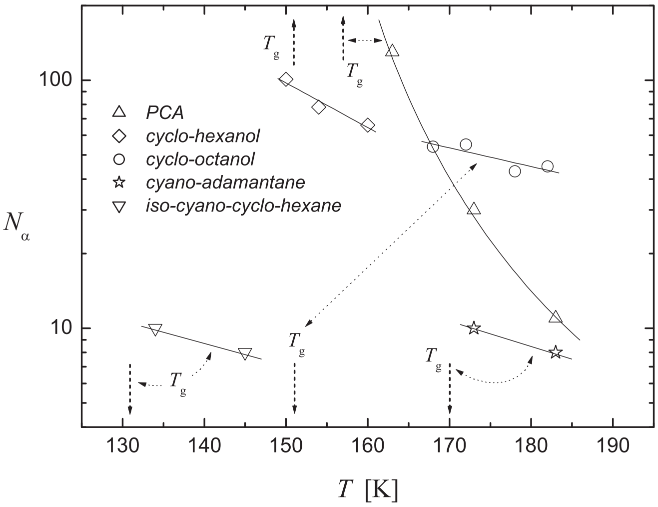

FIG. 2. Cooperativities found for the systems of Table I (LG excluded); the associated glass transition temperatures are also indicated by the dotted arrows. The lines are guides for the eye.

With respect to structural glass formers in general, of which PCA is one example, the temperature dependence of cooperativity in the ODICs considered here (apart from LG, which has been analyzed at just one temperature) seems to be weaker in proximity of their respective T_g's (also the T-dependence of ζ^*, if any, conforms to this trend). Concerning μ_0 we usually find that it slightly increases with temperature, thus following the same trend of Ts_c. The case of Cy-Hex, instead, is special because a significant *decrease* on heating is found for this quantity; hereby, we are inclined to relate this observation to the instability of the Crystal-I phase (wherein orientational relaxation occurs) on heating towards $T \sim 160$ K [35]. In Ref. [34], the significant reduction in amplitude of the α-peak on approaching $T = 200$ K from above, and its disappearance on heating in the interval between 160 K and 200 K, have been ascribed to this instability mechanism too.

Comparison between Cy-Hex and i-Cn-Cy-He close to the respective T_gs suggests that hydrogen bonding interactions enhance cooperativity; the best fitting ζ^* values of Table I support this interpretation (although these systems have similar values of Ts_c in proximity of their T_g, this does not follow directly from the fact that μ_0 is much larger in Cy-Hex, as Eq. (11) would suggest, because the ζ^* values differ significantly in the two cases). If one thinks of cooperativity as the effect of a "drag" accompanying the diffusional motion of a unit, then this picture seems reasonable. However, the arguments of the theory section allow for an interpretation that entirely refers to the pretransitional dynamic regime. Consider indeed that diffusional motion is characterized by very low values of ζ^*, that are reached after the facilitation process has come to completion [14]; Eq. (11), instead, refers to the pretransitional state, where facilitation has not started yet and ζ^* is still large. Recalling the comments about the peculiar character of the apparent extensivity in S, just following Eq. (11), it is immediate to relate the cooperativity to the number of possible values the rearrangement barrier probed by a (constrained) rotating unit may take; in turn, this number depends on how many *mobile* units mutually interact, either as nearest neighbors or through mediation by other units (by construction, this is a necessary consequence of the constraint on $\overline{\Delta\mu}$). In the case of i-Cn-Cy-He the interaction is limited to a reduced number of neighbors, the multiplicity of well depth values lowers, and the same do both the entropy and the threshold energy ζ^*; this motivates a lower cooperativity.

The effect of hydrogen bondings may be also highlighted by comparing Cy-Oct and Cn-Adm. In the temperature range considered for the analyses, these systems have similar values of Ts_c, z and ζ^*; however, quite larger specific cooperativities are found in Cy-Oct as an effect of just μ_0 as, this time, Eq. (11) points out.

On its turn, LG is a system with strong hydrogen bonding interactions. In this case the entropy associated to diffusional motion, i.e., $s_c - \mu_0/T$, is comparable with that of Cy-Oct at the measuring temperatures; in addition, the values of the specific cooperativity, λ, are similar too. However, the number of units initiating the large-scale diffusional motion is significantly larger than in the case of Cy-Oct ($z = 5$ against $z \simeq 1.5$), and, after Eq. (14), this provides a major reason for so high a cooperativity worked out.

V. CONCLUDING REMARKS

We based our analysis focusing on the pretransitional state, an intermediate dynamical regime separating the glass from a condition in which configurational motion is unconstrained. Within the theoretical framework proposed above, it is possible to relate cooperativity to basic ideas concerning the character of the energy landscape in glass formers [44]. The emergence of broad spectral patterns in the dynamical response of amorphous systems is indeed connected to the existence of a mixing entropy, S, that is central in defining the potential of Eq. (8) [the multiplicity of ζ values, giving rise to S as an effect of their random changes, causes a broadening of the spectra which is probed through the analytical expression of ϕ via the term $\nu^* \exp[-z\,\Delta\mu(\zeta)/k_BT]$ in Eq. (13)]. The fact that such an entropy contribution maintains its relevance in a single-unit potential, i.e., that it does not vanish in the infinite size limit (consistently with an appropriate size dependence of the inherent structures' multiplicity), provides an *a posteriori* consistency support for cooperativity.

Concerning the issue whether nonexponentiality in the correlation decay might be or not an intrinsic feature of the relaxing mechanism, as when cooperativities are small, the picture given here points at encompassing all cases into a common view: in any case it is the number of minima (or better, the multiplicity of their depth values) probed by a rearranging unit that matters. In structural glass formers this nonexponentiality is usually depicted as a superposition of contributions from disjointed cooperatively rearranging regions, each of them relaxing with its proper, instantaneous, characteristic time. Here nonexponentiality is still described as a superposition of independent contributions, as is evident from Eq. (13), but its local character, even if influenced by the interaction with neighbors, has by no means been highlighted in our physical interpretation [Eq. (11) and subsequent comment]; this still poses some connection between nonexponentiality and size of the rearranging regions, but no Brownian motion needs be invoked for this.

There are issues left over, a thorough consideration of which this contribution cannot afford. The first is of course the origin of the super-Arrhenian dependence of the central relaxation time. Large rearranging domains do not necessarily imply non-Arrhenian behavior; for instance, LG and Cy-Oct are both highly cooperative, but the T-dependence of the apparent activation energy of the latter is significantly weaker. Other fragile ODICs, e.g., a recently studied succinonitrile-glutaronitrile mixture [45], would be of interest in order to compare with less fragile ones and hopefully figure out, at least, a trend in the fitting parameters highlighting this feature. The topic, however, does not seem to be trivial at the outset, and we must defer it to future work.

Another point deserving attention is the particular behavior of μ_0 as a function of T in the case of Cy-Hex. We have presently no information enough to help drawing conclusions from the results of the above analysis; one can only guess, as a possibility, that the decrease of μ_0 on heating (which may be due to a decrease in the average, steady, energy contribution of the rearranging units) could result from a progressive decoupling between the observed rearranging domains and an environment in which the presence of orientationally ordered regions dominates ever more. These regions, as orientationally frozen, would not intervene in establishing the fluctuating potential wells to which rearrangement is so sensitive, thus the cooperativity would be reduced. In other words, the decrease of N_α on heating would also be enhanced by a genuine confinement effect.

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