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# Small Characteristic Length at the Glass Transition Cooperativity Onset

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**Abstract.** — A fluctuation theory approach to a cooperativity onset of the dynamic glass transition is described. Recent dielectric and heat capacity spectroscopy (HCS) experiments for several random copolymers of n-butyl methacrylate with styrene indicate a steep linear increase of relaxation intensities ( $\Delta\epsilon$ ,  $\Delta C_p$ ) and of square root of cooperativity ( $N_\alpha^{1/2}$ ) as function of temperature below the onset. A quasi continuous description is derived from kinetic molecular randomness. This description can be applied to small cooperativity near the onset. The experimental indications can analytically be reproduced by means of a Landau order parameter expansion adapted to dominance of fluctuation in a free volume approach to the dynamic glass transition. An important parameter of the approach is the minimal cooperativity of order  $N_\alpha^{\min} \approx 1$ . The sharp onset obtained in the extrapolation is associated with the construction of a large conditionality raster. Far below the onset, the size of cooperativity at the glass temperature is theoretically estimated to be of order  $N_\alpha(T_g) \approx 100$  molecules. A new interpretation of the WLF asymptote  $\lg \Omega$  is suggested.

## 1. Introduction

Cooling a glass-forming molecular liquid from high temperatures, far below the terahertz  $\alpha\beta_{\text{fast}}$  splitting temperature further anomalies are regularly observed along the  $\alpha$  dispersion zone = dynamic glass transition: the  $\alpha\beta$  (Johari Goldstein) splitting, or a region where the Stokes Einstein Debye relation becomes violated [1], or a dielectric peculiarity, *e.g.* the  $T_A$  temperature of Fischer [2]. It was suggested [2,3] to connect an anomaly with an onset temperature  $T_{\text{ons}}$  of a typical glass-transition cooperativity in the sense of Adam and Gibbs [4]. Usually, the corresponding onset frequency  $\omega_{\text{ons}}$  is in the mega to gigahertz range and, therefore, not so easily accessible by linear response experiments *e.g.* by shear and heat capacity spectroscopy HCS.

But there are some substances where the onset is in frequency regions that are commonly accessible by HCS ( $C_p^*$ ), dielectric ( $\epsilon^*$ ), and shear linear response methods [5–8]. A steep linear onset of dielectric relaxation intensities was observed in many samples,  $\Delta\epsilon \sim (T_{\text{ons}} - T) \equiv \Delta T$ .

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Such a linearity is also described by a modified Fredrickson simulation [9] that enlarges the fluctuation by means of molecular randomness of barrier heights and interaction parameters of the flipping particle at each computational step. This corresponds to an effective acceleration of the calculations at the cost of loss of high-frequency details.

The existence of a characteristic length  $\xi_\alpha$  for the glass transition cooperativity is a long issue [4, 10–12]. Because of the low density contrast [13] of the thermokinetic pattern [14–16] in the liquid there are at present only indirect possibilities to determine such a length experimentally. One possibility is a fluctuation formula from a free volume approach [10, 14, 16],

$$\xi_\alpha^3 \equiv V_\alpha = k_B T^2 \Delta(1/C_v) / \rho \delta T^2 \approx k_B T_g^2 \Delta C_p / \bar{C}_p^2 \rho \delta T^2, \quad (1)$$

where  $V_\alpha$  is the cooperativity volume (cooperatively rearranging region CRR [4]).  $\Delta C_p$  is the heat capacity step and  $\delta T$  the width of the imaginary part of dynamic heat capacity,  $C_p''$ ; both can be determined by calorimetry [10, 14] *e.g.* by HCS [17].

HCS applied to the substances mentioned can investigate the onset region calorimetrically in a relatively large frequency and temperature interval [17, 18]. From equation (1) we then may determine  $V_\alpha$  or the cooperativity, *i.e.* the number of particles  $N_\alpha$  in one CRR, as a function of  $\Delta T$ . As reported in Section 2,  $N_\alpha^{1/2} \sim \Delta T$  is indicated in several random copolymers of n-butyl methacrylate and styrene, poly (nBMA-*stat*-S).  $N_\alpha$  is the number of average monomer units in one CRR.

The  $N_\alpha^{1/2} \sim \Delta T$  onset relation means that  $N_\alpha$  becomes rather small near  $T_{\text{ons}}$ . This generates two theoretical problems. First, since small  $N_\alpha$  values should be connected with large fluctuation that would smear out any sharp typical temperature, we must ask: how to combine a small characteristic length with a steep cooperativity onset? Second, since small  $N_\alpha$  values should be connected with only few particles in a CRR, being a subsystem independent from others [4], we ask: is there a continuous, phenomenological description of the onset applicable to few particles? This theoretical part is the main aim of the paper and will be presented in Section 3.

## 2. Experimental Indications for a Cooperativity Onset

This section reports on some recent dielectric and heat capacity spectroscopy findings in poly (nBMA-*stat*-S) indicating a cooperativity onset. The experimental details will be published elsewhere [18, 19]. This section is only to give a short experimental background for the theoretical part in Section 3.

According to equation (1) it is  $\Delta C_p$  that indicates the glass transition cooperativity. We expect  $\Delta C_p \rightarrow 0$  when an onset is approached from lower temperatures.

Figure 1 shows the HCS results for the 19% mol styrene copolymer. Assuming that density  $\rho$  and heat conductivity  $\kappa$  have only a bend (and not a disperse step) at the dynamic glass transition, the temperature dispersion  $\delta T$  can be determined from Gauss fits of the  $(\rho \kappa C_p)''$  peaks, and the  $\Delta C_p$  steps from the  $(\rho \kappa C_p)'$  curves (after gauging  $C_p'$  with  $C_p^l$  from differential scanning calorimetry, DSC). The curves of Figure 1 show that  $\delta T$  increases and  $\Delta C_p$  decreases as a function of frequency or, mediated by the maximum of  $C_p''$ ,  $T_{\text{max}}(\omega_{\text{max}})$ , as a function of  $T$ . From the  $\delta T$  and  $\Delta C_p$  trends and equation (1) we see that  $V_\alpha$  decreases with increasing temperatures.

The HCS results for a series of the copolymers are compared with dielectric linear response in Figure 2. The intensities  $\Delta \varepsilon$  and  $\Delta C_p$  and the square root of cooperativity  $N_\alpha^{1/2}$  undoubtedly tend to zero, they are approximately linear functions of temperature, with reasonable significance, and have probably, within the uncertainties of about  $\Delta T^s \approx 10$  K, a common onset for

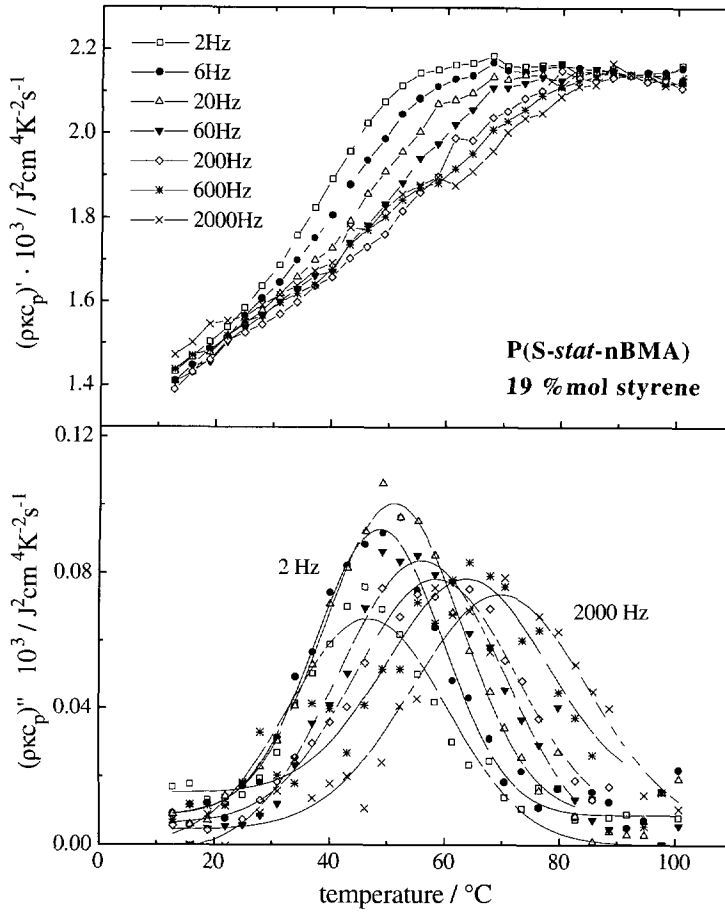


Fig. 1. — Heat capacity spectroscopy HCS results for the random copolymer P(nBMA-*stat*-S) with 19% mol styrene.  $C_p^* = C_p' - iC_p''$  dynamic specific heat,  $\kappa$  heat conductivity,  $\rho$  density. The imaginary peaks are fitted by Gauss curves from which the temperature dispersions  $\delta T$  are calculated.

each polymer composition (Tab. I). Defining  $\Delta T = T_{\text{ons}} - T$ , as mentioned above, we thus have some indication for the following near-onset behavior:

$$\Delta C_p \sim \Delta T, \Delta \varepsilon \sim \Delta T, N_\alpha^{1/2} \sim \Delta T. \quad (2)$$

An  $N_\alpha^{1/2}$  linearity was also obtained in a series of poly(n-alkyl methacrylates) from DSC experiments [20]. The small lengths are supported by the high sensitivity of the  $\alpha/\beta$  splitting scenario to small molecular variations [5].

The inclusion of the 2% styrene sample excludes the possibility that the  $\delta T$  dispersion can be explained by chemical heterogeneity along the chain. On the other hand, the 2% styrene content stabilizes the large sensitivity of homo PnBMA [5] to small non-controllable changes of the splitting region.

Unfortunately there remains a gap of about 20 K between the extrapolated onset and the nearest reliable HCS results, because our HCS set-up is limited to frequencies  $< 2$  kHz and

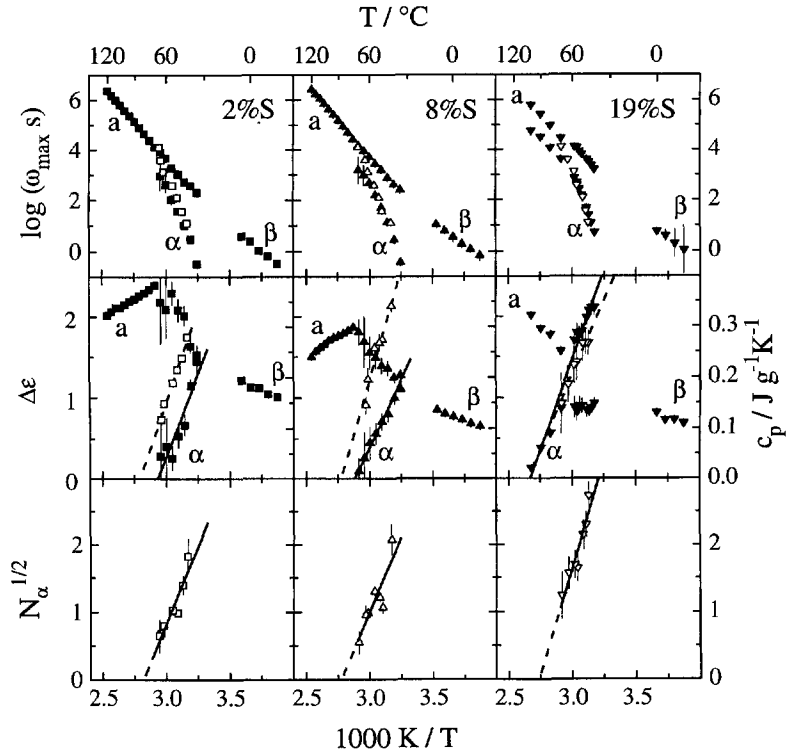


Fig. 2. — Comparison of dielectric spectroscopy with calorimetric HCS results in the  $\alpha\beta$  splitting region for three copolymer samples with 2, 8, and 19% mol styrene. Full symbols are dielectric, open symbols HCS points. Upper part: Arrhenius diagram. The points are loss maxima, the dielectric loss maxima are from a fit with a sum of two HN functions [5]. Middle part: dielectric  $\Delta\epsilon$  and HCS  $\Delta C_p$  intensities. Lower part: square root of the number of (average) monomeric units  $N_\alpha$  in one CRR of volume  $V_\alpha$ . Generally:  $a$  high temperature relaxation,  $\alpha$  cooperative dynamic glass transition,  $\beta$  local relaxation (activated).

Table I. — Onset temperatures from linear regressions of dielectric ( $\Delta\epsilon \rightarrow 0$ ), calorimetric ( $\Delta C_p \rightarrow 0$ ), and cooperativity ( $N_\alpha^{1/2} \rightarrow 0$ ) data of Figure 2.

| sample                   | $T_{\text{ons}}$ |              |                  | average  |
|--------------------------|------------------|--------------|------------------|----------|
|                          | $\Delta\epsilon$ | $\Delta C_p$ | $N_\alpha^{1/2}$ |          |
| 2% S                     | 68               | 85           | 81               | 78       |
| 8% S                     | 74               | 88           | 87               | 83       |
| 19% S                    | 103              | 104          | 93               | 100      |
| uncertainty $\Delta T^s$ | $\pm 10$         | $\pm 10$     | $\pm 10$         | $\pm 10$ |

to sensitivities  $\Delta C_p / \bar{C}_p > 1\%$ . The present findings do not exclude a crossover to a small  $0 < \Delta C_p / \bar{C}_p \lesssim 1\%$  value for the high-temperature  $a$  relaxation beyond the onset,  $T > T_{\text{ons}}$ . The following theory does not consider such a crossover.

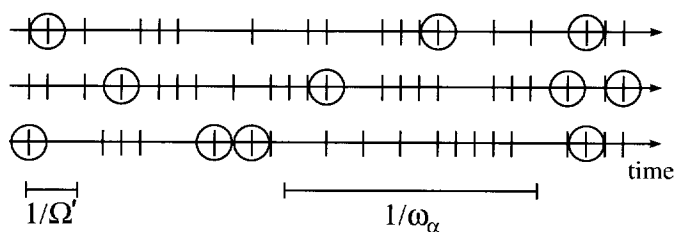


Fig. 3. — Kinetic molecular randomness. Three examples for frequent ( $\Omega'$ ) random chances (+++) and rare (frequency  $\omega_\alpha \ll \Omega'$ ) realizations ( $\ominus$ ) of cooperative rearrangements in case of  $v_\alpha/v_T \ll 1$ .

### 3. Glass Transition Onset Theory

We suggest to use an adapted Landau order parameter construction for a phenomenological description of the equation (2) situation extrapolated to  $\Delta T \rightarrow 0$ : steep linear  $\alpha$  susceptibility onset with small characteristic length. The construction is based on the free volume approach to the dynamic glass transition  $\alpha$  of references [16, 21].

**3.1. KINETIC MOLECULAR RANDOMNESS.** — The thermal velocity of molecules  $v_T$  is of order 100 m/s which results from  $v_T = (3k_B T/m_0)^{1/2}$  with  $m_0$  the mass of the molecule or the monomeric unit. The “velocity” of cooperative rearrangements responsible for the dynamic glass transition,  $v_\alpha$ , is much smaller, of order  $v_\alpha = \xi_\alpha/\tau_\alpha$ , where  $\xi_\alpha$  is the characteristic length of cooperativity (of order nanometers), and  $\tau_\alpha$  a typical rearrangement time ( $\alpha$  relaxation time). For the example  $\xi_\alpha = 1$  nm and  $\tau_\alpha = 10^{-6}$  s we would obtain  $v_\alpha = 10^{-3}$  m/s, *i.e.*  $v_\alpha \ll v_T$ . In the experimental case of Section 2 we have  $v_\alpha$  in the range  $10$  nm/s  $\cdot$   $10$   $\mu$ m/s.

The basic assumption is that for  $v_\alpha \ll v_T$  the high and chaotic thermal velocities generate — during the rearrangement time  $\tau_\alpha$  — a very large number of different local temporary configurations with very much local chances for rearrangements (*cf.* Fig. 3). The frequency of chances is denoted by  $\Omega'$ . These chances can only occasionally and randomly be used for the slow  $\alpha$  cooperative rearrangements (frequency  $\omega_\alpha = \omega$ ). This means that the rearranging path of each molecule has local random events of order one molecule diameter, and the paths of different molecules are different, with random events.

This situation will be called “kinetic molecular randomness” and is thus assumed to be typical for molecular dynamic glass transitions below gigahertz frequency ( $v_\alpha \lesssim 10^{-3}v_T$ ).

This randomness implies two properties of a phenomenological description.

- High level of statistical independence of the cooperative rearrangements, also inside a CRR.
- Independence of the  $\alpha$  rearrangements from other dispersion zones and from high frequency relaxations and vibrations.

This randomness, combined with small CRR length scales, implies further:

- Dominance of fluctuations for describing the dynamic glass transition.

**3.2. KINETIC DEGREES OF FREEDOM FOR DYNAMIC GLASS TRANSITION.** — Trying to apply thermodynamic methods we must define the system under consideration. The smallest subsystem representative for cooperativity is called natural subsystem. Being part of a total system homogeneous at large scale, we must require that the environment of the system cannot supply too much free volume: this would destroy cooperativity. We have therefore at least the condition that the neighbored systems are also cooperative. Interested only in the  $\alpha$  transition we can separate (according to property (b)) the frequency region of the  $\alpha$  dispersion zone.

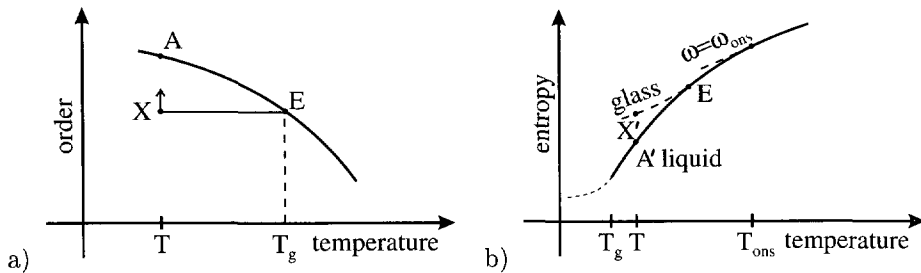


Fig. 4. — a) Structural relaxation according to Simon [22]. E, equilibrium state at glass temperature  $T_g$ . X, glass state at  $T < T_g$  after quenching the E structure.  $X \rightarrow$  structural relaxation to  $A$  = equilibrium state corresponding to  $T$ . b) Translation of Simon's picture to an HCS experiment at  $T$  between  $T_g$  and  $T_{ons}$ .  $X'$  - -E glass zone isochron reaching the equilibrium liquid zone at E ( $\omega = \text{const} < \omega_{ons}$ ). The  $A' \cdots X'$  way would correspond to a glass zone isotherm  $T = \text{const}$  with increasing frequency. The onset situation is also indicated.

A system that represents only one kind of process motion ( $\alpha$  here, cf. also Fig. 4) is called functional system [21]: *a CRR is thus the natural functional  $\alpha$  subsystem.*

A first step for deepening glass-transition thermodynamics to the molecular level is the question of degrees of freedom. One could think, like transition state theory, that more or less the whole group of cooperatively arranging molecules is passing over an energy barrier and, in that sense, has only one degree of freedom in the direction of the action coordinate available.

This is not very likely from the standpoint of kinetic molecular randomness with the distributed chances. From a thermodynamic point of view we can argue similar to Simon [22]. His arguments are related to structural relaxation from the glass state to equilibrium (Fig. 4a),  $X \rightarrow A$  for  $T < T_g$  (see also [21]). Let be the term "way" understood in the thermodynamic sense (change of state), and combine this term with the concept of Goldstein's energy landscape [23]. Then the relaxation  $X \rightarrow A$  is, in the landscape, assumed to be not too far away from the reversible way  $E \cdots A$  in the equilibrium (long times).  $X \rightarrow A$  cannot be connected with a single activation barrier since  $E \cdots A$  is not connected with such a barrier. Instead  $E \cdots A$  is a sequence of stable equilibrium states (at best with varying stability). Irreversibility of  $X \rightarrow A$  is so attributed to the gain of ergodicity during structural relaxation.

Let us translate these arguments to the HCS experiment in the equilibrium liquid state at a given frequency  $\omega < \omega_{ons}$  and temperature  $T < T_{ons}$  (Fig. 4b). We have two zones: the glass zone above and the liquid zone below the dynamic glass transition. Heat capacity corresponds to the relevant slopes in the entropy-temperature diagram. In the glass zone we have  $C_p^g(T)$  corresponding to the slope of the  $\omega$  isochron ( $\omega = \text{const}$ ) at  $X'$ ,  $C_p^l(T)$  in the liquid zone corresponds to the equilibrium slope at  $A'$ ;  $C_p^l > C_p^g$ . If we assume that the kinetic state in  $X'$ , reflected by  $C_p^g$ , corresponds to the equilibrium state in E, then we can argue similar to Simon, with the translation  $E \rightarrow E$ ,  $X \rightarrow X'$ , and  $A \rightarrow A'$ . The result is that there is not a single activation barrier in the sense of transition state theory. By the way, we have also an irreversibility here, reflected by the imaginary part  $C_p''$ , since a periodic heat capacity experiment is a thermodynamic cycle with a mean entropy production per time  $\dot{S}_{irr} = \omega(\Delta_{exp}T)^2 C_p''/2T^2$ , where  $\Delta_{exp}T (< \delta T)$  is the temperature amplitude of the HCS linear-response experiment.

The number of degrees of freedom for the cooperative rearrangement of molecules is therefore an open question. Let us try to define such a degree starting from kinetic molecular randomness and from the proposition that the dynamic glass transition is a kinetic phenomenon.

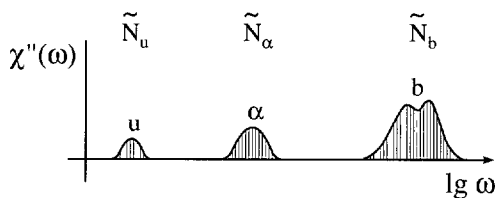


Fig. 5. — Definition of the number of relevant degrees of freedom for functional subsystems by the areas under the  $\chi''(\omega)$  peaks.

In general, linear response from molecular fluctuations is regulated by the fluctuation dissipation theorem, FDT. Our problem is the relation of phenomenological fluctuations of our  $\alpha$  subsystem to the molecules (or, in other words, to the Boltzmann constant  $k_B$  in the FDT). It is generally accepted that all the molecules, in the average over long times, participate with the same “weight” at the glass transition  $\alpha$  (they are “equivalent molecules”); similarly they participate equivalently at the picosecond motions (b) and the ultraslow motions (u, [2]). Therefore, in the average, only a specific part of degrees of freedom ( $\tilde{N}$ ) can be related to  $\alpha$  (or u or b), we have

$$\tilde{N} = \tilde{N}_u + \tilde{N}_\alpha + \tilde{N}_b. \quad (3)$$

The parts  $\tilde{N}_u$ ,  $\tilde{N}_\alpha$ ,  $\tilde{N}_b$  can be determined by the equipartition theorem (a special form of the FDT). Assuming for simplicity that all  $\tilde{N}$  degrees have the same inertia we have  $k_B T = m\bar{v}^2$ , with  $v$  the velocity for this degree. The corresponding velocity autocorrelation function is denoted by  $v^2(t)$ , its spectral density is  $v^2(\omega)$ . Putting

$$\chi''(\omega) \equiv (m/k_B T)\omega v^2(\omega) \geq 0, \quad (4)$$

we have the situation of Figure 5, *i.e.* we have get a peak for each dispersion zone in a  $\chi''$ - $\ln \omega$  diagram, with

$$1 = 2 \int_0^\infty \chi''(\omega) d \ln \omega. \quad (5)$$

This means that  $\tilde{N}$  can be partitioned according to equation (3), where

$$\tilde{N}_\alpha = \tilde{N} \cdot 2 \int_{(\alpha \text{ peak})} \chi''(\omega) d \ln \omega, \quad (6)$$

and analogously for the u and b peaks.  $\tilde{N}_\alpha$  must not be confounded with  $N_\alpha$ , the number of particles in a region of CRR size.

**3.3. QUASI CONTINUOUS DESCRIPTION.** — Since  $\chi''(\omega)$  depends on the temperature (*e.g.* we have  $\chi''_\alpha(\omega) = 0$  for  $T > T_{\text{ons}}$ ),  $\tilde{N}_\alpha$  is a continuous variable, not restricted to integer values for one CRR. In other words, due to kinetic molecular randomness,  $\tilde{N}_\alpha$  is influenced by the relative time interval of the rearranging kink motion mentioned above, and by how the mechanical (true) molecular degrees of freedom are involved in the different dispersion zones u,  $\alpha$ , and b. But there is also some spatial continuity. The equivalence of all molecules for cooperative rearranging means that the  $\tilde{N}_\alpha$  degrees have some collective meaning, and that they are “delocalized” in a CRR, at least in the time scale  $\tau_\alpha$  of the  $\alpha$  dispersion zone.



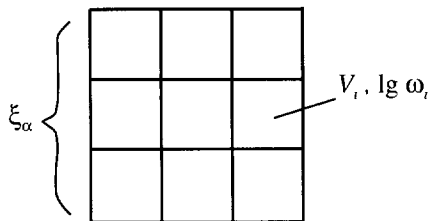


Fig. 6. — Partition of a CRR of size  $V_\alpha = \xi_\alpha^3$  into partial volumes  $V_i$  with partial mobilities  $\lg \omega_i$ .

The properties (a) and (c) of Section 3.1, *i.e.* statistical independence and dominance of fluctuations, allow to sharpen the phenomenological application of the spatial and temporal concepts to lengths smaller than  $\xi_\alpha$  (*e.g.* partial volumes  $V_i$  and local mobilities  $\lg \omega_i$  inside a CRR of volume  $V_\alpha$ , see the example below). This is a consequence of the general property of collectivism: that the relative fluctuation of an ensemble is (much) smaller than the individual fluctuation of the members. That is we shall use collective conceptions down to lengths scales of the molecular diameter, a few angstroms, say. This property will be called “quasi continuous description” [31]. This is a highly abstract level of thermodynamic description for the cooperative  $\alpha$  rearrangements in collective coordinates, based on the three properties (a, b, c) mainly resulting from kinetic molecular randomness for  $v_\alpha \ll v_T$ .

As an example we repeat [16, 21] the description of the kinetic state of a CRR by means of partial frequencies and their fluctuations. We make a partition of a CRR into  $m$  subvolumes  $V_i$  of equal and constant size (Fig. 6):

$$V_\alpha = \sum_{i=1}^m V_i = mV_i. \quad (7)$$

Let us assume that a local mobility  $\lg \omega_i$  can be defined for each partial volume, according to the quasi continuous description, and that, despite of cooperativity, the mobilities  $\lg \omega_i$  for different partial volumes are statistically independent, according to property (b) of Section 3.1. This is, in principle, possible, because statistical independence does not imply physical independence (only: the latter implies the former). Then we have [3, 21], with respect to mobility fluctuations (responsible for a fluctuation spectral density [16]),

$$\omega_\alpha = \text{const} \cdot \omega_1 \cdot \omega_2 \cdot \dots \cdot \omega_m. \quad (8)$$

Let be  $\delta \lg \omega$  the dispersion of the mobility fluctuation. Then we obtain from the statistical independence, equation (8),

$$\delta \lg \omega \equiv \delta \lg \omega_\alpha \sim m^{1/2} \sim N_\alpha^{1/2} \quad (9)$$

Equation (9) means that  $\delta \lg \omega$  increases with the CRR size  $\sim m$ ; larger CRR's contain more partial subvolumes  $V_i$  of given size.

**3.4. CONDITIONS FOR COOPERATIVITY.** — The problem is now to define the  $V_\alpha$  cooperativity in case of statistical independence of fluctuating partial mobilities  $\lg \omega_i$ . Let us assume that we have a coupling between local mobility and local density (free volume) or local structure (“free entropy”). For free volume we can then introduce a “geometrical” coupling between the partial volumes by means of equation (7), or for the partial volume fluctuations,  $\Delta V_i$ ,

$$\Delta V_\alpha = \sum \Delta V_i. \quad (10)$$

Assuming that the statistical independence of mobilities, equation (8), can be transferred to the  $\Delta V_i$  fluctuations we obtain for the dispersions

$$\delta V_\alpha / V_\alpha \ll \delta V_i / V_i \quad \text{for } m \gg 1. \quad (11)$$

This means that, in the average, inside a CRR, enlarging of local density in one  $V_i$  is coupled with diminishing of density in another  $V_j$ ,  $i \neq j$ , (or several others). This property was, when connected with partial mobilities, called *minimal coupling* [16] for describing cooperativity in a CRR.

In other words, in case of cooperativity we have a budget of free volume that is mainly balanced (by Eqs. (10, 11)) within one CRR.

In mathematical terms (with consideration of dominance of fluctuation) we have the following situation: first, for  $T > T_{\text{ons}}$ , there is a large stock of free volume (or entropy), and there is no need for any balance of free volume, *i.e.* there is no additional condition on the mobility as a function of free volume because the latter can freely distributed. In particular, there is no typical length scale because there is no condition on the invariance condition of fluctuation,

$$N\Delta V^2 = \text{inv.} \quad \text{against general subsystem size } N. \quad (12)$$

Second, for  $T < T_{\text{ons}}$ , however, there must be a condition because of the free volume balance by cooperativity. Such a condition may mathematically be formulated by

$$\ln \omega_i = \ln \omega_i(V_i), \quad (13)$$

*i.e.* that the partial mobility fluctuation in a given partial volume  $i$  depends only from the fluctuation of its own partial volume  $i$ , *with taking the balance condition equations (10, 11) into account*. Some consequences of this equation (13) minimal coupling are described in references [16, 21].

Since the balance condition has only a sense inside CRR's this means that such partial volumes have only a sense if they are members of CRR's. One CRR must contain at least two partial volumes,  $m \geq 2$ . Irrespective of the  $V_\alpha$  size we have only cooperativity if we have large domains with CRR's. An isolated CRR would have too many borders open for an attack of free volume destroying cooperativity. This means that the cooperativity is connected with a large "raster of conditionality", *i.e.* large domains of partial volumes, where each of them is member of a CRR with a volume  $V_\alpha$  which latter is independent of the raster domain size.

It seems that large domains of conditionality raster, *i.e.* a long-reaching enchainment of small-scale conditioning environments, is typical for liquids at low temperatures: molecular environments for the molecular glass transition, CRR's themselves for ultra slow modes, or entanglements for the flow transition of polymers.

**3.5. CONDITIONALITY RASTER AT THE ONSET.** — We have, therefore, the following picture (Fig. 7) for the steep equation (2) behavior, or, in the extrapolation  $\Delta T \rightarrow 0$ , for a sharp onset. For large temperatures,  $T > T_{\text{ons}}$ , there are no stable partial volumes since, if existing, they would be dissolved in a sea of an ample stock of free volume.  $T = T_{\text{ons}}$  is the point where we have a stable domain filled with partial volumes all of which are parts of small CRR's. That is we have large domains of partial-volume rasters (that can define a sharp onset temperature) but small characteristic lengths (which alone could not define a sharp onset). This conditionality raster alone cannot define a large physical length except the domain size, so that there is no critical opalescence at  $T_{\text{ons}}$ . The raster is permanent for  $T < T_{\text{ons}}$ , but the average size of the CRR's filling the raster can increase [4, 10, 16].

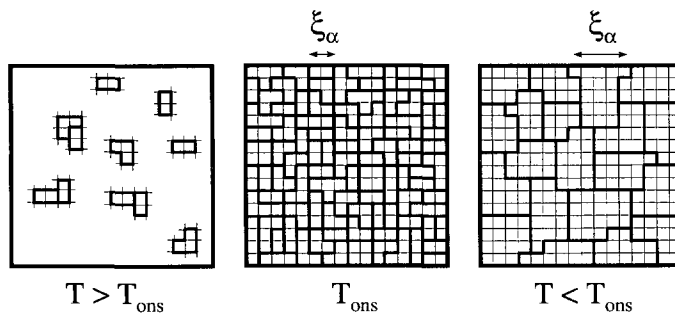


Fig. 7. — The thin squares symbolize the conditionality raster of partial volumes, the bold lines define the fluctuative pattern of cooperatively rearranging regions CRR's (on the raster), with characteristic length  $\xi_\alpha = V_\alpha^{1/3}$ . For  $T > T_{\text{ons}}$  we have at best instable fluctuations with only local rasters.

The occurrence of the CRR's in the conditionality raster breaks the invariance equation (8) below  $T_{\text{ons}}$ , since there are now characteristic sizes  $N_\alpha$  or  $V_\alpha$  in the fluctuation caused at the end by the mobility balance.

**3.6. LANDAU EXPANSION FOR DOMINANCE OF FLUCTUATION.** — The linearity of the functions  $\Delta C_p \sim \Delta T$  and  $N_\alpha^{1/2} \sim \Delta T$  (Eq. (2)) can analytically be obtained from a Landau order parameter expansion dominated by fluctuation. (Recall that we have no large correlation lengths as in an Ornstein Zernike approach to a critical phase transition, and that the fluctuations are not connected with large correlation lengths; *i.e.* there is no need for a Ginsburg criterion, instead *the fluctuations are dominating because the CRR's are so small.*) From the book of Prigogine and Glansdorff [24] we learn that a thermodynamic situation with large fluctuations can also be described by a potential  $f$  that is optimal in equilibrium.

Let  $\eta$  be an “order parameter” and  $\vartheta$  be a “control parameter”. We put the Landau expansion as  $f = \alpha(\vartheta - \vartheta_{\text{ons}})\eta^2 + b\eta^4$ . Then we have for  $\vartheta < \vartheta_{\text{ons}}$ , of course,

$$\eta \sim (\vartheta_{\text{ons}} - \vartheta)^{1/2} \quad (14)$$

For dominance of fluctuation we characterize the caloric situation by the entropy fluctuation of a CRR,  $\Delta S_\alpha$ , and the size of a CRR,  $N_\alpha$ , *i.e.* we put  $f = f(\Delta S_\alpha, N_\alpha)$ . Let be the control and the order parameter respectively defined as

$$\vartheta \sim N_\alpha \quad \text{and} \quad \eta = \overline{\Delta S_\alpha^2} / N_\alpha \sim \Delta C_p, \quad (15)$$

where  $\overline{\Delta S_\alpha^2}$  is the ms entropy fluctuation of one CRR.

The meaning of the term “control” is rather conditional for fluctuation dominance because the usual control parameter, *e.g.* the temperature, is not *a priori* defined in this situation. This will be discussed in the next subsection.

**3.7. THE MAP PROBLEM: INVERSION OF THE PRINCIPLE OF LOCAL EQUILIBRIUM.** — Map problem: dominance of fluctuations means that a common thermodynamic variable of our subsystems (*e.g.* the temperature  $T$ ) is introduced in the description *via* its *internal* spontaneous actual fluctuation  $\delta T$  (related to one CRR *i.e.* to the  $\alpha$  functional subsystem). The kinetic variable  $\lg \omega$  is similarly introduced by a spectral width  $\delta \lg \omega$  of the partial mobility fluctuation, equation (9). Both the temperature and the  $\lg \omega$  fluctuation can be different in different functional subsystems, *i.e.*  $\delta T \equiv \delta T_\alpha \neq \delta T_b \neq \delta T_u$ , and  $\delta \lg \omega \equiv \delta \lg \omega_\alpha \neq \delta \lg \omega_b \neq \delta \lg \omega_u$ . We need, therefore, a mapping ( $\mapsto$ ), denoted by  $\delta T \mapsto \Delta T$

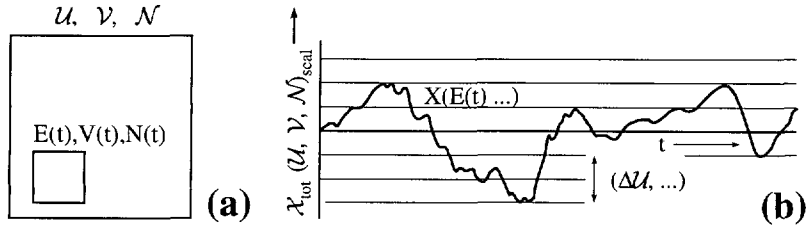


Fig. 8. — a) Subsystem with mechanically simulated quantities  $E(t)$ ,  $V(t)$ ,  $N(t)$ , and total system with thermodynamic variables  $\mathcal{U}$ ,  $\mathcal{V}$ ,  $\mathcal{N}$ . b) Principle of local equilibrium, PLE. Definition of actual thermodynamic variables  $X$  for a fluctuating subsystem. Details, see text.

and  $\delta \lg \omega \mapsto \Delta \lg \omega$  in the example, from internal  $\alpha$  fluctuations  $\delta T$ ,  $\delta \lg \omega$  to common thermodynamic and kinetic (“thermokinetic”) control variables  $T, \lg \omega$  that can be changed  $(\Delta T, \Delta \lg \omega)$  by changing the *external* conditions.

To illustrate the meaning of this map we shortly discuss the inverse map, well known as principle of local equilibrium, PLE [25]. (This principle belongs to the foundations of statistical mechanics and is more than the statement that any subsystem is in local equilibrium with its environment in a situation that permits deviations from the global equilibrium, *e.g.* with a gradient  $\partial T / \partial \mathbf{r} \neq 0$ .) Consider the usual construction producing actual and fluctuating thermodynamic variables from molecular mechanics. Fluctuating means, of course, that the actual values can deviate from the time average. The construction contains four steps [21]. (1) A subsystem larger than natural is mechanically simulated in a computer during the proper time scale. We *determine* from the recordings for any time  $t$ :

$$\begin{aligned} &\text{the volume } V(t) \text{ by geometry,} \\ &\text{the energy } E(t) \text{ from mechanical energy,} \\ &\text{the particle number } N(t) \text{ by counting.} \end{aligned} \quad (16)$$

(2) We *measure* (or calculate from computed average values for many states) the equation of state in a large system, homogeneously added from many such subsystems, so large that all observables have practically sharp values,

$$\mathcal{X}_{\text{tot}} = \mathcal{X}_{\text{tot}}(\mathcal{U}, \mathcal{V}, \mathcal{N}), \quad (17)$$

where  $\mathcal{X}_{\text{tot}}$  stands for thermodynamic variables, such as entropy or temperature, which need not have a direct mechanical interpretation. (3) All extensive observables  $(\mathcal{U}, \mathcal{V}, \mathcal{N})$  of the large system are reduced to the subsystem size by multiplying with  $N/\mathcal{N}$  (scaling according to Fig. 8a). Since the fluctuation of the total system is small we obtain a sharp raster of thermodynamic values, *e.g.*  $\mathcal{X}_{\text{tot}}(\mathcal{U}, \mathcal{V}, \mathcal{N})_{\text{scal}}$  of Figure 8b, of course for equilibrium mean values. Varying externally  $\mathcal{U}$ , or  $\mathcal{V}$ , or  $\mathcal{N}$ , then  $\mathcal{X}$  changes and we obtain a new horizontal (constant) line for the scaled values. (4) Now the subsystem simulations (Eq. (16)) are pursued with time. Each actual value  $E(t)$ ,  $V(t)$ , and  $N(t)$  at time  $t$  is identified with the scaled raster values of  $\mathcal{U}$ ,  $\mathcal{V}$ , and  $\mathcal{N}$  from step (3). The actual off-average or off-equilibrium values of the subsystem then are finally *defined* by this identification,

$$X(t) = X(E(t), V(t), N(t)) \stackrel{\text{def}}{=} \mathcal{X}_{\text{tot}}(\mathcal{U}, \mathcal{V}, \mathcal{N})_{\text{scal, eq.}} \quad (18)$$

The PLE can thus be expressed as follows: the fluctuating thermodynamic variables of a subsystem as a function of the *determined* variables are defined by identification with

the rescaled function thermodynamically *measured* for a large system. This principle permits the temperature — originally defined *via* an equivalence class construction without fluctuation by the Zeroth Law — to be included in the stock of fluctuating thermodynamic variables.

Here we need the inversion of the PLE, defining the controllable, external temperature or temperature differences (*e.g.*  $\Delta T = T_{\text{ons}} - T$ ) from a functional subsystem situation dominated *e.g.* by internal temperature fluctuation  $\delta T$ :  $\delta T \mapsto \Delta T$ , and mobility fluctuation  $\delta \lg \omega$ :  $\delta \lg \omega \mapsto \Delta \lg \omega$ .

As an example for this map we shortly repeat the derivation of the WLF equation from  $\alpha$  fluctuations [16, 21, 26]. From equation (9),  $\delta \lg \omega_\alpha \equiv \delta \lg \omega \sim N_\alpha^{1/2}$ , and from  $\delta T_\alpha \equiv \delta T \sim N_\alpha^{-1/2}$  — temperature being an intensive variable — we have

$$\delta T \delta \lg \omega = \text{const} \quad (19)$$

where const means the independence from  $N_\alpha$ . Taking  $N_\alpha$  to be the most (sharper: the only) important variable [4], we have the following differential-geometric problem for a  $\delta T \mapsto \Delta' T$  map (where  $\Delta' T$  is, for the moment, an arbitrary external temperature difference): what are the integral curves in a  $\lg \omega$ - $T$  diagram that are consistent with equation (19)? Under some physically simple conditions the answer obtained is WLF: this is a set of hyperbolas with common asymptotes  $\lg \omega = \lg \Omega = \lg \Omega_\alpha$  and  $T = T_\infty = T_{\infty\alpha}$  (Vogel temperature for  $\alpha$ ),

$$(T - T_\infty) \lg \frac{\Omega}{\omega} = (T_0 - T_\infty) \lg \frac{\Omega}{\omega_0}, \quad (20)$$

where  $(T_0, \omega_0)$  is a reference point. Equation (20) is the WLF equation. The usual WLF constants are the distances of the reference point to the asymptotes in the  $\lg \omega$ - $T$  diagram:  $c_1^0 = \lg(\Omega/\omega_0)$ ,  $c_2^0 = T_0 - T_\infty$ .

We see that the PLE in thermokinetic terms can be called WLF scaling or, in its local variant, temperature-time superposition, TTS,

$$\delta T / \delta \lg \omega = \Delta T / \Delta \lg \omega |_{\text{along WLF}} = (T - T_\infty) / \lg(\Omega/\omega), \quad (21)$$

where  $\Delta T / \Delta \lg \omega$  is here the slope along the WLF curve. Equation (21) is visualized in Figure 9.

*Remark:* the Gibbs distribution uses, by means of a large heat reservoir, a Zeroth Law temperature that cannot fluctuate. This ensemble is too restricted for describing all the relevant fluctuations of our CRR subsystem. Nevertheless it seems an interesting question if the temperature obtained from the map is equal to the canonical system temperature from the Gibbs distribution. A first answer is yes since the WLF equation is actually observed. A second check would be the actual observation of the temperature dependence of the fluctuating free volume,  $v_f \sim x^{2/x}$ , ( $x$  see below Eq. (28), [16]), which relation was solely obtained from fluctuation. This function shows exhausting of free volume at an exhausting temperature,  $T_E$ , somewhere near the middle between Vogel and onset temperature.

**3.8. LINEAR ONSET FROM THE LANDAU EXPANSION.** — Let us now return to the Landau expansion of the onset problem. We start from the statistical independence in the quasi continuous description, equation (9):  $N_\alpha \sim (\delta \lg \omega_\alpha)^2$ , where  $\delta \lg \omega_\alpha$  is the mobility dispersion of a CRR. From the first definition, equation (15),  $\vartheta \sim N_\alpha$ , we have

$$N_\alpha \sim \vartheta \sim (\delta \lg \omega_\alpha)^2. \quad (22)$$

The PLE inversion map  $\mapsto$  transforms the internal  $\alpha$  mobility dispersion into an external mobility change,  $\delta \lg \omega \mapsto \Delta \lg \omega$ . From the temperature-time superposition equation (21)

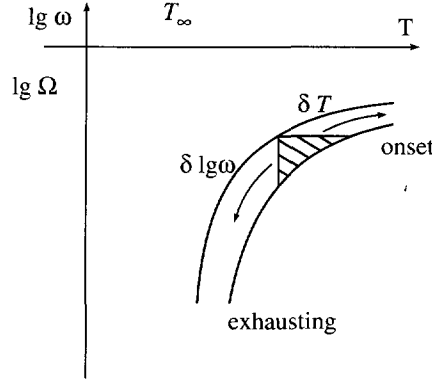


Fig. 9. — Visualization of the WLF map from internal  $\alpha$  fluctuation to external variables,  $\delta \lg \omega \mapsto \Delta \lg \omega$  or  $\lg \omega$ , and  $\delta T \mapsto \Delta T$  or  $T$ . The invariance condition (19) means that the area of the hatched triangle is constant with respect to a shift *along* the two WLF hyperbolas; their distance characterizes the dispersion (broadness) of the guided dispersion zone.

we transform the change of mobility to a real temperature change,  $\Delta \lg \omega \sim \Delta T$ . This is applied to the onset difference.  $\Delta T = T_{\text{ons}} - T$ , and we have  $\vartheta_{\text{ons}} - \vartheta \sim (\Delta T)^2$ . From equation (22) we obtain

$$N_{\alpha}^{1/2} \sim T_{\text{ons}} - T \quad (23)$$

where we formally put  $N_{\alpha, \text{ons}} = 0$  in the quasi continuous description. Using now the Landau equation (14) we obtain from the second equation (15),  $\eta \sim \Delta C_p$  with  $\vartheta_{\text{ons}} - \vartheta \sim (\Delta T)^2$ ,

$$\Delta C_p \sim T_{\text{ons}} - T \quad (24)$$

with  $\Delta C_{p, \text{ons}} = 0$ . Equations (23, 24) describe the experimental indications of equation (2) and Figure 2. Using the fluctuation of dielectric polarization instead of  $\overline{\Delta S_{\alpha}^2}$ , we would also obtain the third indication,  $\Delta \epsilon \sim T_{\text{ons}} - T$ .

**3.9. ESTIMATION OF THE PROPORTIONALITY CONSTANT.** — Now we shall estimate the proportionality constant of equation (23). First we gauge equation (22). Let  $m_{\text{ons}}$  be the minimal number of partial volumes of a CRR, *i.e.*  $m_{\text{ons}} \geq 2$ , and  $N_1$  the number of particles in a reasonable partial volume. The product

$$N_{\alpha}^{\text{min}} = m_{\text{ons}} N_1 \quad (25)$$

(number of particles of a CRR needed for a *minimal cooperativity*) is invariant against the  $V_i$  size of the Figure 6 partition. Let  $\delta_0 \lg \omega$  be the dispersion of the  $\alpha$  transition at the onset. (For a Debye relaxation (Lorentz line for  $\alpha$  relaxation at the onset), as compared with a  $\lg \omega$  Gauss function at the half-width, we would have  $\delta_0 \lg \omega \equiv \delta_0 \log_{10} \omega = 0.49 \approx 1/2$ .) Then, gauging with these onset values, we obtain from equation (22)

$$(N_{\alpha}/m_{\text{ons}} N_1)^{1/2} = \delta \lg \omega / \delta_0 \lg \omega. \quad (26)$$

From the TTS equation (21) we obtain in the onset vicinity, after using the  $\delta \lg \omega \mapsto \Delta \lg \omega$ ,  $\delta T \mapsto \Delta T$  map from fluctuation to external variables,

$$N_{\alpha}^{1/2} = (m_{\text{ons}} N_1)^{1/2} \frac{\lg(\Omega/\omega_{\text{ons}})}{\delta_0 \lg \omega} \frac{(T_{\text{ons}} - T)}{T_{\text{ons}} - T_{\infty}} \quad (27)$$

Using a reduced temperature between onset and Vogel temperature,

$$x = (T - T_{\infty}) / (T_{\text{ons}} - T_{\infty}), \quad 0 \leq x \leq 1. \quad (28)$$

we obtain near the onset ( $1 - x \ll 1$ )

$$N_{\alpha}^{1/2} = A(1 - x) \quad (29)$$

with the following reduced proportionality constant  $A$

$$A = (m_{\text{ons}} N_1)^{1/2} \frac{\lg(\Omega/\omega_{\text{ons}})}{\delta_0 \lg \omega} = (N_{\alpha}^{\text{min}})^{1/2} \frac{\lg(\Omega/\omega_{\text{ons}})}{\delta_0 \lg \omega} \quad (30)$$

Putting  $m_{\text{ons}} = 2$ ,  $N_1 = 1$  (*i.e.* a minimal cooperativity  $N_{\alpha}^{\text{min}} = 2$  particles),  $\lg(\Omega/\omega_{\text{ons}}) = 3$  (*e.g.* a general onset of order GHz for  $\Omega$  in the THz region), and  $\delta_0 \lg \omega = 1/2$  (Lorentz line  $\alpha$  onset) we would obtain the estimation  $A = 6\sqrt{2} \approx 10$ .

The experimental values obtained in our copolymers are  $\lg(\Omega/\omega_{\text{ons}}) = 4 \pm 0.5$ , independently from composition although  $\Omega$  changes by four decades.  $\delta_0 \lg \omega \approx 2 \pm 0.5$ ,  $N_{\alpha}^{\text{min}} \approx 1.5 \pm 0.5$  monomeric units, and  $A \approx 3.0 \pm 1.5$ , *i.e.* our copolymer  $A$  is somewhat smaller than from the general estimation.

The main uncertainty of estimation comes from  $N_1$ , the number of particles in one reasonable partial volume for the onset region (remember  $m_{\text{ons}} \geq 2$ ). The smallest experimental  $N_{\alpha}$  values of Figure 2 are of order 1 monomeric PnBMA unit, *i.e.*  $V_{\alpha} \approx 0.1 \text{ nm}^3$ . The number of mechanical degrees of freedom for this monomeric unit is much larger than one. It is therefore possible to have  $N_1 < 1$ . This would explain  $A < 10$  for our copolymers, even for  $\lg(\Omega/\omega_{\text{ons}}) > 3$  with moderate deviation from three. The  $A$  constant also decreases for larger onset dispersions  $\delta_0 \lg \omega$ . Because of the nonlocal aspects in the quasi continuous description,  $N_{\alpha}^{\text{min}} \approx 1$  does not mean to define cooperativity inside one monomeric unit.  $A > 10$  is obtained for polymers with a complex main transition such as polyisobutylene [27].

The  $A$  values seem to be, from the arguments leading to equation (30), not too material specific, in particular when considered in one substance class.

Our approach is only consistent for  $N_{\alpha} \geq N_{\alpha}^{\text{min}}$ , of course. This corresponds to a distance  $\Delta T \gtrsim 20 \text{ K}$  to the onset. We have no predictions for  $N_{\alpha} < N_{\alpha}^{\text{min}}$  and for a possible cross-over to a  $T > T_{\text{ons}}$  dispersion which could hide the extrapolated sharpness of the Landau expansion, equation (14) for  $\vartheta \rightarrow 0$ .

**3.10. ESTIMATION OF COOPERATIVITY AT THE EXHAUSTING AND THE GLASS TEMPERATURE.** — Using a certain  $A$  value we can finally try to estimate the size of a CRR at the glass temperature. Assume that the one  $A$  constant determines this size in the full WLF range [32]. From WLF, *i.e.* equations (20, 19, 9), we obtain [26] in  $d = 3$  dimensions

$$N_{\alpha}^{1/2} \sim (T - T_{\infty})^{-1} \sim 1/x. \quad (31)$$

Interpolating [18] between equations (29) and (31) we get

$$N_{\alpha}^{1/2} = A(1 - x)/x. \quad (32)$$

Let be the exhausting temperature  $T_E$  [16] in the middle between  $T_{\infty}$  and  $T_{\text{ons}}$ , *i.e.*  $x_E = 1/2$ . Then we obtain

$$N_{\alpha}(T_E) = A^2. \quad (33)$$

The  $A$  constant is between 3 and 15 for fourteen glass-forming substances [27]. This means that  $N_{\alpha}(T_E)$  is between 10 and 225 molecules or monomeric units. Below  $T_E$  we expect larger

$N_\alpha$  values than calculated from equation (32) because additional sources of free volume must be opened.

Let us now assume that we have no exhausting between  $T_{\text{ons}}$  and the glass temperature  $T_g$ , *i.e.* that we have only one piece of WLF equation between  $T_{\text{ons}}$  and  $T_g$ .  $T = T_g$  means  $x = x_g = (T_g - T_\infty)/(T_{\text{ons}} - T_\infty)$ . Introduce a fragility measure by

$$F = T_g/(T_g - T_\infty) \quad (34)$$

(observe: for one WLF region we have  $F = m/\lg(\frac{\Omega}{\omega_g}) = m/c_1^g$  with  $m \equiv d \lg \omega_\alpha^{-1}/d(T_g/T) |_{T=T_g}$  and  $c_1^g$  the first WLF constant with  $T_0 = T_g$  as reference). Typical values are  $F = 2 \cdot 4$  for strong and  $F = 5 \cdot 7$  for fragile [28] liquids. We obtain from equation (32)

$$N_\alpha^{1/2}(T_g) = A \frac{T_{\text{ons}} - T_g}{T_g - T_\infty} = AF \frac{T_{\text{ons}} - T_g}{T_g} \quad (35)$$

If the ratio  $(T_{\text{ons}} - T_g)/T_g = \text{const}$ , *e.g.*  $\text{const} \approx 0.2$ , then

$$N_\alpha^{1/2}(T_g) \approx AF \cdot 0.2. \quad (36)$$

The size of this cooperativity is larger for higher fragility, as observed [10]. A typical value obtained for  $A = 10$  and  $F = 5$  is  $N_\alpha^{1/2}(T_g) \approx 10$ , *i.e.*

$$N_\alpha(T_g) \approx 100. \quad (37)$$

Assuming 10 molecules per  $\text{nm}^3$  we obtain  $V_\alpha(T_g) \approx 10 \text{ nm}^3$ , *i.e.*  $\xi_\alpha \approx 2 \text{ nm}$ , also higher for higher fragilities.

For the series of our copolymers the ratio  $(T_{\text{ons}} - T_g)/T_g$  is not constant, and  $N_\alpha(T_g)$  strongly increases with the styrene content [20].

#### 4. Discussion and Conclusion

A phenomenological theory is obtained in this paper that describes the cooperativity  $N_\alpha$  (as indirectly obtained from Eq. (1)) in the temperature range between about 20 K below the onset and the exhausting or glass temperature. The onset itself is probably covered by a crossover to a weaker cooperativity for a high-temperature  $\alpha$  process above  $T_{\text{ons}}$ . The onset can only be extrapolated from the experiments with an uncertainty of  $\Delta T^s \approx 10 \text{ K}$  by means of the linear relations equation (2).

To attack the glass-transition onset problem a rather abstract phenomenological concept of natural functional subsystems [21] is used. The abstractness corresponds to several widespread “canonical” properties of the experimental findings for the (structural) glass transition. *E.g.* the selection of the main variables for our concept: temperature ( $T$ ) and mobility ( $\lg \omega$ ), exactly corresponds to the original WLF generalization [29]: “This [WLF] treatment is quite independent of the nature of the relaxation spectrum and the time dependence of mechanical and electrical properties [we would add calorimetric ones]; it appears to be equally applicable to narrow and broad relaxation distributions”. Our concept can also explain other canonical properties of the dynamic glass transition: WLF scaling itself [26], Kohlrausch (KWW) relaxation function [16], and exhausting of a fluctuating free volume [16] describing the deviations from one total WLF equation. The concept also leads to an interpretation of the Vogel temperature as the roughness of Goldstein’s relevant energy landscape [21]. The WLF limit frequency  $\lg \Omega$  can be interpreted [19] as a “kinetic roughness” of this landscape, expressed by  $\lg \Omega'$ , the logarithm of the chance frequency (+++) in the Figure 3 molecular randomness.



*Conditions* for cooperativity are analyzed in a situation that is dominated by fluctuations and statistical independence (within and between the CRR's). This dominance is originated by the small cooperativity scale and by the concept of kinetic molecular randomness (Fig. 3) assumed to be acting for molecular glass transitions below the gigahertz range.

If near the onset the mean CRR temperature fluctuation is larger than the  $T_{\text{ons}}$  uncertainty,  $\delta T > \Delta T^s$ , we have a problem: this  $\delta T$  characterizes the fluctuating thermokinetic nanoheterogeneity in the glass-forming liquid [16] and does not easily allow to define a sharp (*i.e.*  $\Delta T^s < \delta T$ ) onset temperature. Such an onset temperature rather demands a large scale of something to suppress local fluctuations of  $T_{\text{ons}}$ . In case of phase transitions the sharp critical temperature follows from large diverging correlation lengths, and a sharp first-order phase transition (*e.g.* melting) is connected with large phase domains.

A resolution of this sharpness problem is formally obtained by the construction of a conditionality raster that can define a large raster domain size without a large characteristic length of the CRR's inside the domains. The extrapolated sharp onset is identified with the temperature where the conditionality raster domains (and not the CRR's) become large (Fig. 7). The sharpness of the onset is then obtained analytically from a Landau order parameter expansion adapted to the large fluctuations resting on the *smallness* of characteristic length for the CRR's.

The objection to apply phenomenological concepts down to very small CRR's with only a few particles is tried to be settled by arguments for a quasi continuous description of Section 3.3 [31].

We obtain a theory that is consistent for  $N_\alpha \gtrsim N_\alpha^{\text{min}}$ , *i.e.* beyond about 20 K below the onset, and describes the linear experimental equation (2) indications. The immediate  $T_{\text{ons}}$  vicinity is delegated to a crossover to a supposedly small cooperativity of the  $a$  process for  $T > T_{\text{ons}}$ .

As a by-product, our new approach opens, for the first time, a way to estimate absolute values of the size of glass transition cooperativity theoretically. Supposing that it is the onset parameters that also determine the characteristic length far below the onset,  $N_\alpha$  at  $T_g$  is obtained of order 100 molecules (or monomeric units), and the characteristic length is of order 2 nanometers. These estimations correspond to the experimental values obtained from the calorimetric formula (1).

The cause for the large  $\Omega/\omega_{\text{ons}}$  ratio,  $\lg(\Omega/\omega_{\text{ons}}) \approx 4$  for our copolymers, is the necessity of molecular kinetic randomness for functioning of molecular cooperativity with minimal coupling (Sects. 3.3 and 3.4).

We speculate about the following scenario for the dynamic glass transition. According to a conjecture of Stickel *et al.* [30] the  $\alpha$  dispersion zone consists of two (or perhaps more) more or less different WLF pieces with narrow crossovers. Consider the WLF piece where the cooperativity starts with a small number of entities,  $N_\alpha^{\text{min}}$ . The cooperativity onset ( $T_{\text{ons}}$ ,  $\lg \omega_{\text{ons}}$ ) is at the upper end, but far below the extrapolated WLF frequency  $\Omega$ . The cooperativity increases with falling temperatures according to equation (32), down to the exhausting temperature  $T_E$  far above the extrapolated Vogel temperature (Fig. 9). At  $T_E$  we expect a crossover to another WLF (or Arrhenius) process with different  $\lg \Omega$  and  $T_\infty$  parameters, probably a longer [21] glass transition using new sources of free volume from mechanisms neighbored to the original dynamic glass transition. The validity of the original WLF equation is thus restricted to the piece interval  $(T_{\text{ons}}, \lg \omega_{\text{ons}}) \cdot (T_E, \lg \omega_E)$ , with  $\lg \omega_{\text{ons}} < \lg \Omega$  and  $T_E > T_\infty$ . The  $\lg \Omega$  and  $T_\infty$  WLF constants must therefore be interpreted as actual properties of the WLF piece considered, and not as asymptotes that could in principle be accessible by the cooperative process.

## Acknowledgments

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- [31] Note added in proof. The quasi-continuous space concept can be specified as follows. Let us assume that the cooperativity chances with high frequencies of order  $\Omega'$  are provided by smaller groups than a CRR (with total rearrangements of frequency  $\omega_\alpha$ ). Define a space point for any chance by the center of gravity for this smaller group. Since there are many chances in the  $\tau_\alpha = 1/\omega_\alpha$  time scale (Fig. 3) we have many space points for a quasi-continuous description of the cooperative rearrangements in a CRR. This allows the extension of the description to very small parts of a CRR and to very small CRR's itself, *e.g.* in the onset region.
- [32] Note added in proof. If the whole  $N_\alpha(T)$  function can actually be described by one single  $\Lambda$  constant, then we would have an important theoretical consequence. The cooperativity development to lower temperature would be predetermined by minimal cooperativity  $N_\alpha^{\min}$  under onset conditions, *i.e.* the enlargement of cooperativity beyond  $N_\alpha^{\min}$  could not introduce new elements not contained in the minimal variant.