

# Cage rattling does not correlate with the local geometry in molecular liquids

S. Bernini

*Dipartimento di Fisica “Enrico Fermi”, Università di Pisa,  
Largo B.Pontecorvo 3, I-56127 Pisa, Italy*

F. Puosi

*Laboratoire Interdisciplinaire de Physique, Université Joseph Fourier Grenoble,  
CNRS, 38402 Saint Martin d’Hères, France*

D. Leporini\*

*Dipartimento di Fisica “Enrico Fermi”, Università di Pisa,  
Largo B.Pontecorvo 3, I-56127 Pisa, Italy and  
IPCF-CNR, UOS Pisa, Italy*

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## Abstract

Molecular-dynamics simulations of a liquid of short linear molecules have been performed to investigate the correlation between the particle dynamics in the cage of the neighbors and the local geometry. The latter is characterized in terms of the size and the asphericity of the Voronoi polyhedra. The correlation is found to be poor. In particular, in spite of the different **Voronoi volume** around the end and the inner monomers of a molecule, all the monomers exhibit coinciding displacement distribution when they are caged (as well as at longer times during the structural relaxation). It is concluded that the fast dynamics during the cage trapping is a non-local collective process involving monomers beyond the nearest neighbours.

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\*Electronic address: [dino.leporini@df.unipi.it](mailto:dino.leporini@df.unipi.it)

## I. INTRODUCTION

Global order is virtually absent in systems like glasses and liquids. On the contrary, local order is present in both disordered and ordered phases [1–4]. A crucial aspect of the solidification leading to a glass is that it is associated only to subtle static structure changes, e.g. the static structure factor  $S(q)$ , measuring the spatial correlations of the particle positions, does not show appreciable changes on approaching the glass transition (GT). The absence of apparent static correlations distinguishing a glass and a liquid motivated research where the focus is on **the dynamical facilitation by mobile particles on the nearby ones to trigger their kinetics** [5]. **The facilitation approach is seen as an attempt to put in a more microscopic way the concept of free volume by assuming that geometrical constraints act at the level of kinetic rules with no reference to the microscopic interactions which are responsible for them** [6].

A different line of thought suggests that structural aspects matter in the dynamical behaviour of glassforming systems. This includes the Adam-Gibbs derivation of the structural relaxation [7, 8] - built on the thermodynamic notion of the configurational entropy [9] -, the mode-coupling theory [10] and extensions [11], the random first-order transition theory (RFOT) [12], the frustration-based approach [13], as well as the so-called elastic models [14, 15]. The search of a link between structural ordering and slow dynamics motivated several studies in liquids [16–19], colloids [20–22] and polymeric systems [20, 23–28].

On approaching the glass transition, particles are trapped by the cage of the first neighbors more effectively and the average escape time, i.e. the structural relaxation time  $\tau_\alpha$ , increases from a few picoseconds up to thousands of seconds [6, 29–32]. The caged particles are not completely immobilized by the surroundings but they wiggle with mean-square amplitude  $\langle u^2 \rangle$  on the picosecond time scale  $t^*$ .  $\langle u^2 \rangle$  is related to the Debye-Waller factor which, assuming harmonicity of thermal motion, takes the form  $\exp(-q^2 \langle u^2 \rangle / 3)$  where  $q$  is the absolute value of the scattering vector. Henceforth,  $\langle u^2 \rangle$  will be referred to as short-time mean-square displacement (ST-MSD). The temporary trapping and subsequent escape mechanisms lead to large fluctuations around the averaged dynamical behavior with strong heterogeneous dynamics [6] and leads to non-exponential relaxation and aging [33]. Despite the huge range of time scales older [34] and recent theoretical [35–41] studies addressed the rattling process in the cage to understand the structural relaxation - the escape process - gaining support from numerical [8, 15, 41–62] and experimental works on glassforming liquids [41, 63, 64] and glasses [38, 65–70].

Recently, extensive molecular-dynamics (MD) simulations evidencing the universal correlation between the structural relaxation time  $\tau_\alpha$  and  $\langle u^2 \rangle$  were reported in polymeric systems [52–54], binary atomic mixtures [55], colloidal gels [56] and antiplasticized polymers [41] and compared with the experimental data concerning several glassformers in a wide fragility range ( $20 \leq m \leq 191$ ) [52, 55, 57, 59]. One major finding was that states with equal ST-MSD  $\langle u^2 \rangle$  have equal relaxation times  $\tau_\alpha$  too. For polymers states with equal ST-MSD show also equal chain reorientation rate [53, 54] and diffusivity [54]. Diffusion scaling was also observed in atomic mixtures [55]. More recently, the influence of free volume and the proper time scales to observe the genuine fast dynamics have been considered [58, 59] as well as the breakdown of the Stokes-Einstein (SE) law [60], the relation with the elastic modulus [15] and the spatial extension of the involved particle displacements at short-times [61, 62].

Insight into the scaling between relaxation and fast dynamics is provided by the particle displacement distribution, i.e. the incoherent, or self part, of the van Hove function  $G_s(r, t)$  [71, 72]. The interpretation of  $G_s(r, t)$  is direct. The product  $G_s(r, t) \cdot 4\pi r^2 dr$  is the probability that the particle is at a distance between  $r$  and  $r + dr$  from the initial position after a time  $t$ . In terms of  $G_s(r, t)$  the scaling property is expressed by stating that, if two physical states, say X and Y, are characterized by the *same* displacement distribution  $G_s(r, t^*)$  at the rattling time  $t^*$ , they also exhibit the *same* distribution at long times, e.g. at  $\tau_\alpha$  [54, 55]:

$$G_s^{(X)}(r, t^*) = G_s^{(Y)}(r, t^*) \iff G_s^{(X)}(r, \tau_\alpha) = G_s^{(Y)}(r, \tau_\alpha) \quad (1)$$

Eq.1 holds even in the presence of very strong dynamical heterogeneity where both diffusive and jump-like dynamics are observed [54] and, in this respect, is consistent with previous conclusions that the long-time dynamical heterogeneity is predicted by the fast heterogeneities [47, 73].

The present paper aims at investigating by molecular-dynamics (MD) simulations if the cage dynamics on the fast time scale  $t^*$  correlates with the local order in a molecular liquid. Local order will be characterized in terms of two measures, i.e. the volume and the asphericity of the Voronoi polyhedron (VP) surrounding a tagged particle. VP asphericity has been analyzed also in water [74–76], small molecules [77], hard spheres [78] and polymers [41, 45, 79, 80]. For a VP with  $V_v$  volume and  $A_v$  surface the asphericity is defined as:

$$a_v = \frac{(A_v)^3}{36\pi (V_v)^2} - 1 \quad (2)$$

The asphericity vanishes for spheres, and is positive for not spherical objects. It will be shown that

the correlation between ST-MSD and the two measures of the local order is quite poor pointing to the non-local character of the fast motion of a particle within the cage of its neighbors.

The paper is organized as follows. In Sec. II the molecular model and the MD algorithms are presented. The results are discussed in Sec. III. Finally, the main conclusions are summarized in Sec. IV.

## II. METHODS

Molecular-dynamics (MD) simulations of a melt of fully-flexible linear chains are performed. The interacting potential between non-bonded monomers reads as:

$$U_{p,q}(r) = \frac{\varepsilon}{q-p} \left[ p \left( \frac{\sigma^*}{r} \right)^q - q \left( \frac{\sigma^*}{r} \right)^p \right] + U_{cut} \quad (3)$$

Changing the  $p$  and  $q$  parameters does not affect the position  $r = \sigma^* = \sqrt[6]{2} \sigma$  and the depth of the potential minimum  $\varepsilon$ . The constant  $U_{cut}$  is chosen to ensure  $U_{p,q}(r) = 0$  at  $r \geq 2.5 \sigma$ . Notice that  $p = 6, q = 12$  yields the familiar Lennard-Jones (LJ) potential. The bonded monomers interact by a potential which is the sum of the LJ potential and the FENE (finitely extended nonlinear elastic) potential [81]:

$$U_{FENE}(r) = -\frac{1}{2} k R_0^2 \ln \left( 1 - \frac{r^2}{R_0^2} \right) \quad (4)$$

where  $k$  measures the magnitude of the interaction and  $R_0$  is the maximum elongation distance. The parameters  $k$  and  $R_0$  have been set to  $30 \varepsilon / \sigma^2$  and  $1.5 \sigma$  respectively. We study systems of about 2000 monomers at different density  $\rho$ , temperature  $T$  and  $p, q$  parameters. Each state is labeled by the multiplet  $\{\rho, p, q, T\}$ . All quantities are in reduced units: length in units of  $\sigma$ , temperature in units of  $\varepsilon / k_B$  and time in units of  $\sigma \sqrt{\mu / \varepsilon}$  where  $\mu$  is the monomer mass. We set  $\mu = k_B = 1$ .  $NPT$  and  $NVT$  ensembles have been used for equilibration runs, while  $NVE$  ensemble has been used for production runs for a given state point ( $NPT$ : constant number of particles, pressure and temperature;  $NVT$ : constant number of particles, volume and temperature;  $NVE$ : constant number of particles, volume and energy).  $NPT$  and  $NVT$  ensembles are studied by the extended system method introduced by Andersen [82] and Nosé [83]. The numerical integration of the augmented Hamiltonian is performed through the multiple time steps algorithm, reversible Reference System Propagator Algorithm (r-RESPA) [84]. We investigate three sets of states of a melt of trimers ( $M = 3$ ):

- Set A: (1.015,7,15,1.05), (1.09,8,12,1.4)
- Set B: (1.016,7,15,0.7), (1.086,6,12,0.7)
- Set C: (0.984,6,12,0.33), (1.086,6,12,0.63)

The states of each set have equal ST-MSD  $\langle u^2 \rangle$  and structural relaxation time  $\tau_\alpha$  (see Sec. III A). In addition we also study a melt of decamers ( $M = 10$ ) with  $\rho = 1.086$ ,  $T = 0.65$  with LJ interaction between non-bonded monomers exhibiting a structural relaxation time  $\tau_\alpha \simeq 152$ .

### III. RESULTS AND DISCUSSION

#### A. Correlation between cage rattling and structural relaxation

A central quantity of interest is the distribution of the monomer displacements which is accounted for by the self-part of the van Hove function  $G_s(\mathbf{r}, t)$  [71, 72]:

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)] \right\rangle \quad (5)$$

In isotropic liquids, the van Hove function depends on the modulus  $r$  of  $\mathbf{r}$ . The second moment of  $G_s(r, t)$  is related to the mean square displacement (MSD):

$$\langle r^2(t) \rangle = 4\pi \int_0^\infty r^2 G_s(r, t) r^2 dr \quad (6)$$

In order to characterize the cage fast dynamics we consider the MSD evaluated at the characteristic time scale  $t^*$  which is defined by the condition that the derivative  $\Delta(t) \equiv \partial \log \langle r^2(t) \rangle / \partial \log t$  is minimum at  $t^*$ , i.e.  $t^*$  is the time when MSD changes the concavity in the log-log plot [52, 53].  $t^*$  is a measure of the trapping time of the particle and corresponds to a few picoseconds in actual units. In the present model  $t^* \simeq 1$  in MD units, irrespective of the physical state [52], and ST-MSD is defined as  $\langle u^2 \rangle = \langle r^2(t = t^*) \rangle$ .

The spatial Fourier transform of the self-part of the van Hove function yields the self-part of the intermediate scattering function (ISF)  $F_s(q, t)$  [72]:

$$F_s(q, t) = \int G_s(r, t) e^{-iq \cdot r} dr \quad (7)$$

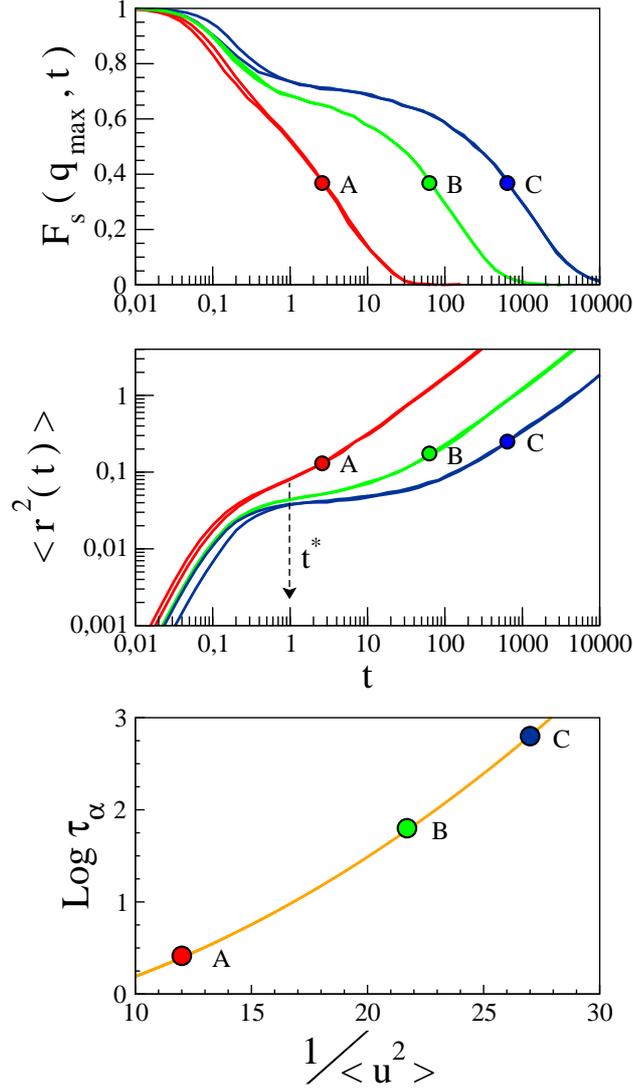


FIG. 1: Top: ISF of the states of the sets A,B,C; the dots mark the structural relaxation time  $\tau_\alpha$ . Middle: monomer MSD of the states of the sets A,B,C.  $\langle u^2 \rangle$  is the short-time MSD (ST-MSD) evaluated at the time  $t^*$  when MSD changes the concavity in the log-log plot. Bottom: location of the sets of states in the master curve  $\log \tau_\alpha$  vs  $\langle u^2 \rangle^{-1}$  (orange line) [52]. Note that ISF and MSD of states of the same set coincide from  $t \simeq t^*$  onward.

which, in an isotropic liquid, depends only on the modulus of the wavevector  $q = |\mathbf{q}|$ . ISF is a useful tool to investigate the rearrangements of the spatial structure over the length scale  $2\pi/q$ . Since we are interested in the structural relaxation of the cage surrounding the tagged particle, ISF is evaluated at  $q = q_{\max}$ , where the maximum of the static structure factor is located. Accordingly, the structural relaxation time  $\tau_\alpha$  is defined by the equation  $F_s(q_{\max}, \tau_\alpha) = e^{-1}$ .

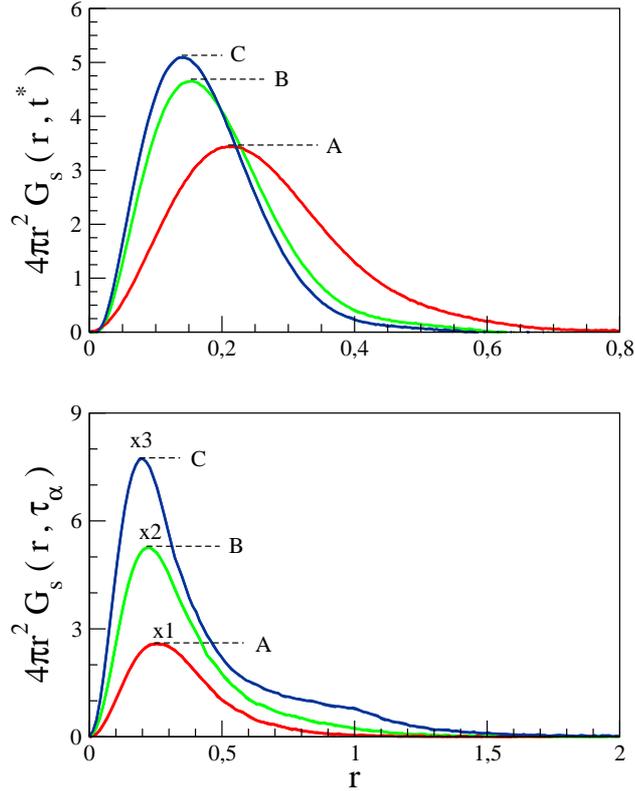


FIG. 2: Particle displacement distribution of the states of the sets A,B,C evaluated at the rattling time  $t = t^*$  (top) and the structural relaxation time  $t = \tau_\alpha$  (bottom). Each curve results from the virtually *perfect* superposition of the curves pertaining to the different states of each set. Note the characteristic bump at  $r \sim 1$  due to the more apparent jump dynamics occurring for the states of the C set.

Fig.1 shows ISF (top) and MSD (middle) of the sets A,B,C. In agreement with Eqs.1, 6, 7, it is seen that states with equal ST-MSD  $\langle u^2 \rangle$  have equal  $\tau_\alpha$  [52, 54, 55]. Even more, states of the same set have coinciding MSD and ISF from times about  $t^*$  onward. This points to a strong correlation between the picosecond rattling motion in the cage and the structural relaxation (the deviations in the ballistic regime at very short times are due to the different temperatures). Careful studies show that the correlation is also present in the diffusive regime, i.e. states with equal ST-MSD have equal diffusivity [54, 55].

The coincidence of MSD and ISF of states with equal  $\tau_\alpha$  for  $t \gtrsim t^*$  reflects the scaling of the self-part of the van Hove function, Eq.1. This is shown in Fig 2 which evidences the coincidence of  $G_s(r, t)$  with  $t = t^*$  (top) and  $t = \tau_\alpha$  (bottom) for states belonging to the same set. Note that the coincidence of  $G_s(r, \tau_\alpha)$  of the states of the sets C extends up to  $r \sim 1$  (the monomer diameter)

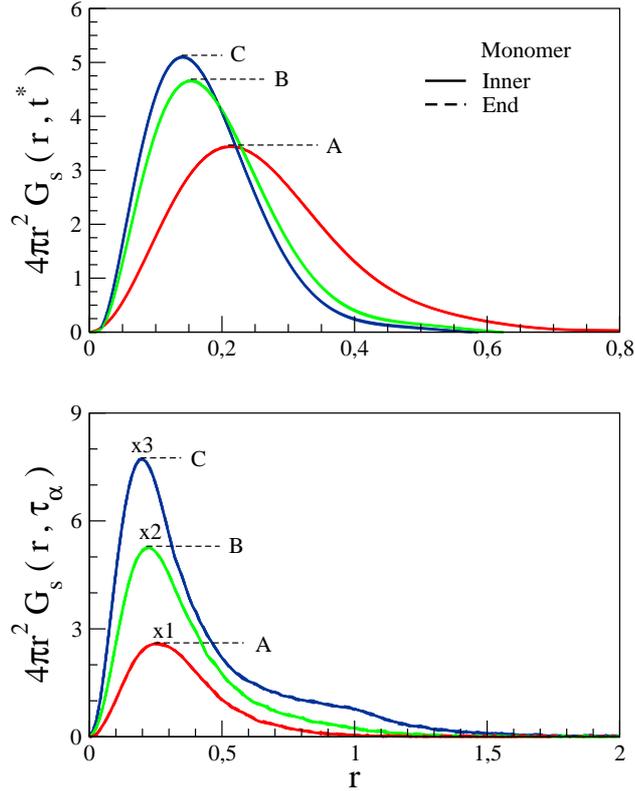


FIG. 3: Particle displacement distribution of the inner and outer monomers of the trimers for the sets of states A,B,C at the rattling time  $t = t^*$  (top) and the structural relaxation time  $t = \tau_\alpha$  (bottom). For each set of states all the curves are coinciding, namely, the displacement distribution depends on neither the monomer position along the chain nor, for a given relaxation time, the state itself.

where the characteristic bump due to the jump dynamics is apparent .

The displacement distribution in Fig.2 is averaged over *all* the monomers. We now prove that, actually, the shape of the distribution is independent of the specific monomer. To this aim, Fig.3 shows the van Hove functions of the inner and the outer monomers of the trimers for the sets of states A,B,C. It is seen that they are virtually coincident at both short ( $t = t^*$ ) and long ( $t = \tau_\alpha$ ) times and *independent* of the physical state for a given relaxation time.

## B. Local geometry: Voronoi polyhedra

To characterize the local geometry of the neighborhood of a tagged particle we perform a space tessellation in terms of the Voronoi polyhedra. Given a particular arrangement of the monomers,

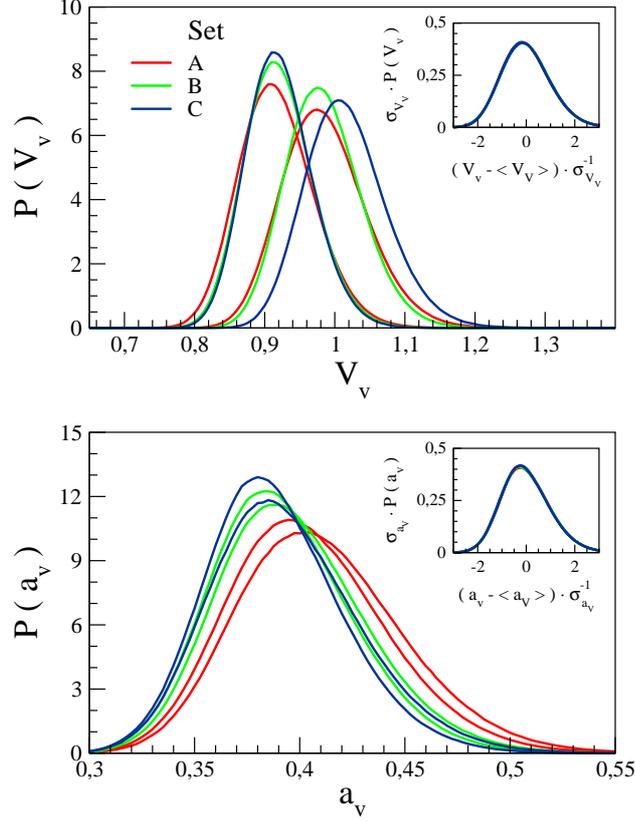


FIG. 4: Distribution of Voronoi polyhedra's volume  $V_v$  (top) and asphericity  $a_v$  (bottom), for set A (red curves), B (green curves) and C (blue curves). **The insets show that a single master curve is obtained by shifting the distributions by the average and scaled by the root-mean-square deviation, as noted before [45].**

the Voronoi polyhedron (VP) surrounding a tagged monomer encloses all the points which are closer to it than to any other one. In particular, we are interested in both their volume  $V_v$  and their asphericity  $a_v$ , Eq.2.

Fig.4 shows the distributions of the volume (top) and the asphericity (bottom) of the VPs for the three sets of states under investigation. It is apparent that states of the same set do not have the same distribution of local geometries. Remind that states belonging to the same set have coinciding monomer displacement distribution at both short and long times (Fig.2). **The insets of Fig.4 show that the distributions of both the volume and the asphericity of the VPs collapse to a single master curve by following Starr et al [45]. This suggests the existence of a single underlying distribution.**

To provide more insight, we considered the C set of states and analyzed in a separate way the

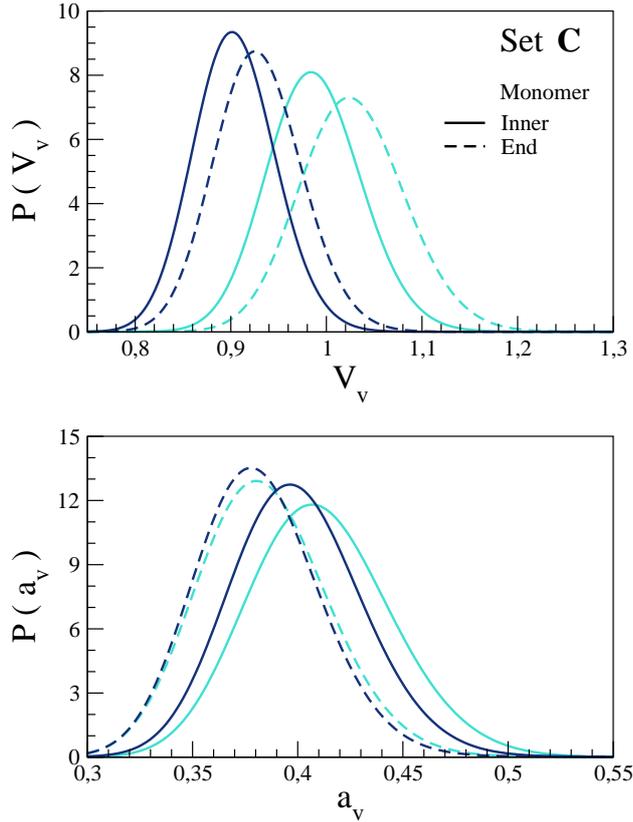


FIG. 5: Distribution of the Voronoi polyhedra's volume  $V_v$  (top) and asphericity  $a_v$  (bottom) for the inner and the end monomers of the trimers of the states of the set C. Thick blue: (1.086,6,12,0.63), light blue : (0.984,6,12,0.33).

volume and the asphericity distributions of the end and the inner monomers. The results are plotted in Fig.5. It is seen (top panel) that end monomers have extra **Voronoi volume** with respect to the inner monomers, as it is well known since long times [85] and observed in previous MD work [86]. Furthermore, VPs of the end monomers are more spherical. In spite of the different local geometries around the end and the inner monomers their displacement distributions are identical at both short and long times (Fig.3). This results is in agreement with MD studies on a 2D glass-forming alloy showing that having a larger **Voronoi volume** does not cause a particle to exhibit larger amplitude fluctuations in position [87].

It must be pointed out that the above results are not limited to trimers - where some correlation between the motion of the end and the inner monomers arises from their direct bonding - but it is also observed in longer molecules. In fact, Fig.6 shows that also in a melt of decamers the displacement distribution of the two end and the two innermost monomers *coincide*, whereas the

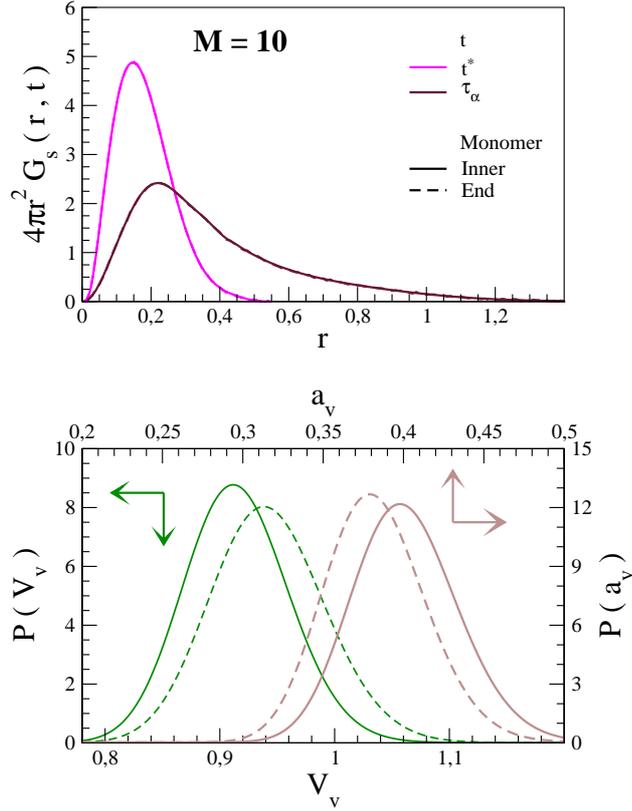


FIG. 6: Dynamics and local geometry of the two end and the two innermost monomers of a single chain molecule for the melt of decamers. Top: distribution of the monomer displacements at short and long times. Notice that the displacement distributions of the end and the inner monomers are coinciding. Bottom: distributions of the VPs volume (green) and asphericity (brown).

local geometry around them is *different*.

Our findings suggest that the fast motion of a particle within the cage of the neighbors is a non-local process. We propose that it results from the collective motion of particles in a region extending more than the first neighbours region. In fact, equal-time, i.e. simultaneous, particle motion correlating over the next-nearest neighbours even at the short (picosecond) time scales has been evidenced [61, 62]. **This is consistent with the evidence of quasi-local soft modes, i.e. with an extended component, in MD simulations of 2D binary mixtures and the finding that the regions of motion of the quasi-local soft modes exhibit striking correlation with the regions of high Debye-Waller factor [47–49].**

The conclusion that the influence of structure on dynamics is weak on short length scale has been reached before by Berthier and Jack, who predicted that it becomes much stronger on long

length scale [88]. From this respect, the evidence of strong correlations between the (long wavelength) elasticity and the fast and slow dynamics deserves further consideration [15, 89].

#### IV. CONCLUSIONS

A supercooled liquid of linear molecules has been investigated by MD simulations. The emphasis is on the possible correlation between the local order and the dynamics at short and long times, as probed by cage rattling and structural relaxation, respectively. Two measures of the local order, i.e. the VP volume and asphericity have no clear correlation with both fast and slow dynamics. In particular, it is found that the excess **Voronoi volume** surrounding the end monomers does not enhance their dynamics neither at short nor at long times. It is concluded that fast dynamics is a non-local process extending farther than the first neighbor shell.

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- [1] P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, *Phys. Rev. Lett.* **75**, 2714 (2005).
  - [2] A. R. Kansal, S. Torquato, and F. H. Stillinger, *Phys. Rev. E* **66**, 041109 (2002).
  - [3] T. Aste, *J. Phys.: Condens. Matter* **17**, S2361 (2005).
  - [4] S. Bernini, F. Puosi, M. Barucco, and D. Leporini, *J. Chem. Phys.* **139**, 184501 (2013).
  - [5] D. Chandler and J. P. Garrahan, *Annu. Rev. Phys. Chem.* **61**, 191 (2010).
  - [6] L. Berthier and G. Biroli, *Rev. Mod. Phys.* **83**, 587 (2011).
  - [7] G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
  - [8] J. Dudowicz, K. F. Freed, and J. F. Douglas, *Adv. Chem. Phys.* **137**, 125 (2008).
  - [9] J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.* **28**, 373 (1958).
  - [10] W. Götze, *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory* (Oxford University Press, Oxford, 2008).
  - [11] K. Chen, E. J. Saltzman, and K. S. Schweizer, *Annu. Rev. Condens. Matter Phys.* **1**, 277 (2010).
  - [12] V. Lubchenko and P. G. Wolynes, *Annu. Rev. Phys. Chem.* **58**, 235 (2007).
  - [13] G. Tarjus, S. A. Kivelson, Z. Nussinov, and P. Viot, *J. Phys.: Condens. Matter* **17**, R1143 (2005).
  - [14] J. C. Dyre, *Rev. Mod. Phys.* **78**, 953 (2006).
  - [15] F. Puosi and D. Leporini, *J. Chem. Phys.* **136**, 041104 (2012).
  - [16] S. Capponi, S. Napolitano, and M. Wübbenhorst, *Nat. Commun.* **3**, 1233 (2012).

- [17] S. Singh, M. D. Ediger, and J. J. de Pablo, *Nat. Mater.* **12**, 139 (2013).
- [18] T. Speck, A. Malins, and C. P. Royall, *Phys. Rev. Lett.* **109**, 195703 (2012).
- [19] A. Barbieri, G. Gorini, and D. Leporini, *Phys. Rev. E* **69**, 061509 (2004).
- [20] J. C. Conrad, F. W. Starr, and D. A. Weitz, *J. Phys. Chem. B* **109**, 21235 (2005).
- [21] C. P. Royall, S. R. Williams, T. Ohtsuka, and H. Tanaka, *Nat. Mater.* **7**, 556 (2008).
- [22] M. Leocmach and H. Tanaka, *Nat. Commun.* **3**, 974 (2012).
- [23] T. S. Jain and J. de Pablo, *J. Chem. Phys.* **122**, 174515 (2005).
- [24] C. R. Iacovella, A. S. Keys, M. A. Horsch, and S. C. Glotzer, *Phys. Rev. E* **75**, 040801(R) (2007).
- [25] N. C. Karayiannis, K. Foteinopoulou, and M. Laso, *J. Chem. Phys.* **130**, 164908 (2009).
- [26] B. Schnell, H. Meyer, C. Fond, J. Wittmer, and J. Baschnagel, *Eur. Phys. J. E* **34**, 97 (2011).
- [27] M. Asai, M. Shibayama, and Y. Koike, *Macromolecules* **44**, 6615 (2011).
- [28] L. Larini, A. Barbieri, D. Prevosto, P. A. Rolla, and D. Leporini, *J. Phys.: Condens. Matter* **17**, L199 (2005).
- [29] M. D. Ediger and P. Harrowell, *J. Chem. Phys.* **137**, 080901 (2012).
- [30] C. A. Angell, K. L. Ngai, G. B. McKenna, P. McMillan, and S. W. Martin, *J. Appl. Phys.* **88**, 3113 (2000).
- [31] P. G. Debenedetti and F. H. Stillinger, *Nature* **410**, 259 (2001).
- [32] R. Richert, *J. Phys.: Condens. Matter* **14**, R703 (2002).
- [33] C. Monthus and J.-P. Bouchaud, *J. Phys. A: Math. Gen.* **29**, 3847 (1996).
- [34] A. Tobolsky, R. E. Powell, and H. Eyring, in *Frontiers in Chemistry*, edited by R. E. Burk and O. Grummit (Interscience, New York, 1943), vol. 1, pp. 125–190.
- [35] C. A. Angell, *Science* **267**, 1924 (1995).
- [36] R. W. Hall and P. G. Wolynes, *J. Chem. Phys.* **86**, 2943 (1987).
- [37] J. C. Dyre, N. B. Olsen, and T. Christensen, *Phys. Rev. B* **53**, 2171 (1996).
- [38] L.-M. Martinez and C. A. Angell, *Nature* **410**, 663 (2001).
- [39] K. L. Ngai, *Phil. Mag.* **84**, 1341 (2004).
- [40] K. L. Ngai, *J. Non-Cryst. Solids* **275**, 7 (2000).
- [41] D. S. Simmons, M. T. Cicerone, Q. Zhong, M. Tyagic, and J. F. Douglas, *Soft Matter* **8**, 11455 (2012).
- [42] C. A. Angell, *J. Am. Chem. Soc.* **86**, 117 (1968).
- [43] S. V. Nemilov, *Russ. J. Phys. Chem.* **42**, 726 (1968).
- [44] J. Shao and C. A. Angell, in *Proc. XVIIth International Congress on Glass, Beijing* (Chinese Ceramic

Societ, 1995), vol. 1, pp. 311–320.

- [45] F. Starr, S. Sastry, J. F. Douglas, and S. Glotzer, Phys. Rev. Lett. **89**, 125501 (2002).
- [46] P. Bordat, F. Affouard, M. Descamps, and K. L. Ngai, Phys. Rev. Lett. **93**, 105502 (2004).
- [47] A. Widmer-Cooper and P. Harrowell, Phys. Rev. Lett. **96**, 185701(4) (2006).
- [48] A. Widmer-Cooper, H. Perry, P. Harrowell, and D. R. Reichman, Nature Physics **4**, 711 (2008).
- [49] A. Widmer-Cooper, H. Perry, P. Harrowell, and D. R. Reichman, J.Chem.Phys. **131**, 194508 (2009).
- [50] H. Zhang, D. J. Srolovitz, J. F. Douglas, and J. A. Warren, Proc. Natl. Acad. Sci. USA **106**, 7735 (2009).
- [51] X. Xia and P. G. Wolynes, PNAS **97**, 2990 (2000).
- [52] L. Larini, A. Ottochian, C. De Michele, and D. Leporini, Nature Physics **4**, 42 (2008).
- [53] A. Ottochian, C. De Michele, and D. Leporini, J. Chem. Phys. **131**, 224517 (2009).
- [54] F. Puosi and D. Leporini, J.Phys. Chem. B **115**, 14046 (2011).
- [55] F. Puosi, C. D. Michele, and D. Leporini, J. Chem. Phys. **138**, 12A532 (2013).
- [56] C. De Michele, E. Del Gado, and D. Leporini, Soft Matter **7**, 4025 (2011).
- [57] A. Ottochian, F. Puosi, C. D. Michele, and D. Leporini, Soft Matter **9**, 7890 (2013).
- [58] A. Ottochian and D. Leporini, J. Non-Cryst. Solids **357**, 298 (2011).
- [59] A. Ottochian and D. Leporini, Phil. Mag. **91**, 1786 (2011).
- [60] F. Puosi and D. Leporini, J. Chem. Phys. **136**, 211101 (2012).
- [61] F. Puosi and D. Leporini, J. Chem. Phys. **136**, 164901 (2012).
- [62] F. Puosi and D. Leporini, J. Chem. Phys. **139**, 029901 (2013).
- [63] U. Buchenau and R. Zorn, Europhys. Lett. **18**, 523 (1992).
- [64] L. Andreozzi, M. Giordano, and D. Leporini, J. Non-Cryst. Solids **235**, 219 (1998).
- [65] T. Scopigno, G. Ruocco, F. Sette, and G. Monaco, Science **302**, 849 (2003).
- [66] A. P. Sokolov, E. Rössler, A. Kisliuk, and D. Quitmann, Phys. Rev. Lett. **71**, 2062 (1993).
- [67] U. Buchenau and A. Wischnewski, Phys. Rev. B **70**, 092201 (2004).
- [68] V. N. Novikov and A. P. Sokolov, Nature **431**, 961 (2004).
- [69] V. N. Novikov, Y. Ding, and A. P. Sokolov, Phys.Rev.E **71**, 061501 (2005).
- [70] S. N. Yannopoulos and G. P. Johari, Nature **442**, E7 (2006).
- [71] P. A. Egelstaff, *An introduction to the liquid state* (Clarendon Press, Oxford, 1992), 2nd ed.
- [72] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids, 3rd Ed.* (Academic Press, 2006).
- [73] Note that  $t^*$  is one order of magnitude shorter than the times considered in ref. [47].

- [74] P. Jedlovsky, J. Chem. Phys. **111**, 5975 (1999).
- [75] K. T. Wikfeldt, M. Leetmaa, A. Mace, A. Nilsson, and L. G. M. Pettersson, J. Chem. Phys. **132**, 104513 (2010).
- [76] G. Stirnemann and D. Laage, J. Chem. Phys. **137**, 031101 (2012).
- [77] G. Ruocco, M. Sampoli, and R. Vallauri, J. Chem. Phys. **96**, 6167 (1992).
- [78] W. P. Krekelberg, V. Ganesan, and T. M. Truskett, J. Chem. Phys. **124**, 214502 (2006).
- [79] M. Sega, P. Jedlovsky, N. N. Medvedev, and R. Vallauri, J. Chem. Phys. **121**, 2422 (2004).
- [80] D. Rigby and R. J. Roe, Macromolecules **23**, 5312 (1990).
- [81] G. S. Grest and K. Kremer, Phys. Rev. A **33**, 3628 (1986).
- [82] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
- [83] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
- [84] M. E. Tuckerman, B. J. Berne, and G. J. Martyna, J. Chem. Phys. **97**, 1990 (1992).
- [85] F. Bueche, *Physical Properties of Polymers* (Interscience, New York, 1962).
- [86] A. Barbieri, D. Prevosto, M. Lucchesi, and D. Leporini, J. Phys.: Condens. Matter **16**, 6609 (2004).
- [87] A. Widmer-Cooper and P. Harrowell, J. Non-Cryst Solids **352**, 5098 (2006).
- [88] L. Berthier and R. L. Jack, Phys. Rev. E **76**, 041509 (2007).
- [89] F. Puosi and D. Leporini, arXiv:1108.4629.