Specific heat anomaly in a supercooled liquid with amorphous boundary conditions

Daniel A. Mártin,[1, 2] Andrea Cavagna,[3] and Tomás S. Grigera[1, 4, 5, *]

[1]*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CONICET and Facultad de Ciencias Exactas,*
Universidad Nacional de La Plata, c.c. 16, suc. 4, B1904DPI La Plata, Argentina
[2]*Departamento de Ciencias Básicas, Facultad de Ingeniería,*
Universidad Nacional de La Plata, 1900 La Plata, Argentina
[3]*Istituto Sistemi Complessi (ISC), Consiglio Nazionale delle Richerche (CNR),*
UOS Sapienza, Via dei Taurini, 19, 00185 Roma, Italy
[4]*CCT CONICET La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina*
[5]*Departamento de Física, Universidad Nacional de La Plata, c.c. 67, 1900 La Plata, Argentina*
(Dated: April 15, 2015)

We study the specific heat of a model supercooled liquid confined in a spherical cavity with amorphous boundary conditions. We find the *equilibrium* specific heat has a cavity-size-dependent peak as a function of temperature. The cavity allows us to perform a finite-size scaling (FSS) analysis, which indicates the peak persists at a finite temperature in the thermodynamic limit. We attempt to collapse the data onto a FSS curve according to different theoretical scenarii, obtaining reasonable results in two cases: a "not-so-simple" liquid with nonstandard values of the exponents α and ν, and random first-order theory (RFOT), with two different length scales.

In fragile glassformers, the relaxation time increases faster than the Arrhenius law as temperature is lowered [1]. This implies that the effective barrier to relaxation grows on cooling, which leads to expect concomitant structural, and perhaps thermodynamic, changes. Though not universally accepted, the idea that a thermodynamic transition may underlie the dynamic glass transition is old and at the core of random first-order theory (RFOT) and other theoretical approaches [2]. The question of the existence of a transition is open; in fact *structural* changes accompanying the slowdown have been found only recently [3–11], after more than a decade of study of dynamic correlations [12, 13].

The most general tools for probing structural correlations are the "order-agnostic" methods —which include patch correlations [7, 14], finite-size scaling (FSS) [15, 16], point-to-set (PTS) [17] and its related correlations— which do not need knowledge of the order parameter. Calculation of PTS correlations involves the study of confined systems, and in part for this reason a growing number of studies of liquids under various confined geometries have been reported, mainly cavities with amorphous boundary conditions (explained below) [3, 10, 18–21], "cavities" with open directions [21, 22] and systems with pinned particles [9, 21, 23]. These investigations have focused mostly on density correlations, from which a correlation length can be extracted.

Here we report numerical results on the specific heat C_V of a system confined under amorphous boundary conditions (ABCs), therefore combining the ABCs and standard FSS approaches [24]. We find an anomalous peak as a function of temperature. The algorithm we use (swap Monte Carlo (MC) [25]) provides a complete sampling of configuration space at all the temperatures we report, so the peak is completely unrelated to the usual anomalies caused by the system falling out of equilibrium. We use FSS to study the changes of this *thermodynamic* anomaly as the cavity is enlarged, and our results indicate that it remains at a finite temperature in the thermodynamic limit. This is further evidence of the structural changes happening in supercooled liquids, and supports the existence of a thermodynamic transition.

We study the soft-sphere binary mixture of ref. [26] with size ratio 1.2 and unit density. To confine with ABCs, a spherical cavity of radius R is created in an equilibrium configuration from a periodic boundary conditions (PBCs) system at temperature T, introducing a hard wall that conserves density and composition inside the cavity [3, 20, 27]. Inside particles evolve with swap MC [25] at the same temperature, while outside particles are held fixed. The specific heat is computed through energy fluctuations, $C_V = \overline{[\langle E^2 \rangle - \langle E \rangle^2]}/(MT^2)$, where E is the energy, M the number of cavity (free) particles, and the overline means average over different realizations of the BCs. All results correspond to the (meta)*equilibrium supercooled liquid.* We used the energy time correlation function (checking for aging and finite-time effects) to estimate a correlation time and ensure that all relevant quantities were computed using runs lasting more than 100 relaxation times (including, self-consistently, the energy correlation). We used the bond orientation order parameter Q_6 [28] to exclude samples that showed signs of crystallization and could give a spurious contribution to the liquid C_V. Note that equilibration of small cavities is not problematic since with swap Monte Carlo smaller cavities are faster (not slower) than larger ones [29]. For detailed description of simulation and equilibration procedures and crystallization checks, see SM [30].

Fig. 1 shows the specific heat per mobile particle for ABCs for several cavity sizes (from 28 to 2000 mobile
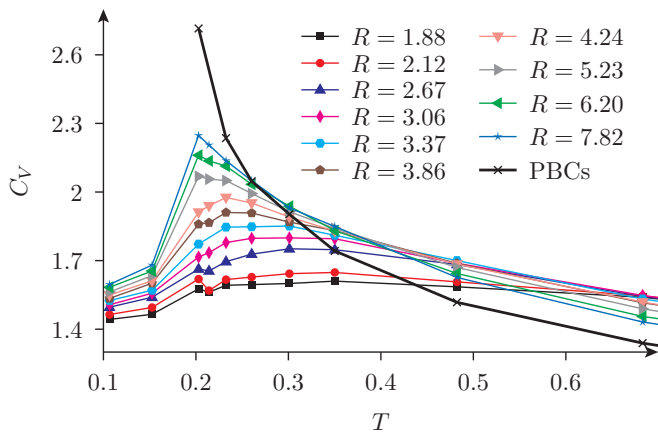
FIG. 1. (color online) Specific heat vs. T for amorphous boundary conditions (ABCs). Error bars omitted for clarity; the absolute error is bounded by 0.03. PBCs data are for a system of $N = 8192$ particles, where C_V can be measured down to $T \approx 0.2$ (see SM for details).

particles), displaying a peak. The peak is not due to the system going out of equilibrium, or to crystal formation. For classical liquids, C_V is expected to be monotonically decreasing with temperature (as has been shown for a large number of liquid models [33, 34] and follows from the phonon theory of liquids [35]): in this sense, the observed peak is an anomaly. A similar anomaly has been reported before [25, 36], although in rather small systems and without a FSS analysis.

In the simplest scenario, the qualitative origin of this anomalous peak can be explained if we accept that the effect of the border penetrates into the cavity as far as a length-scale $\lambda(T)$, and that this penetration length increases for lower T [20]. At very high T the effect of the boundary is weak ($\lambda(T)$ is very small) and the C_V of the liquid inside the cavity follows its bulk behavior (in our case well described at high T by the Rosenfeld-Tarazona law $C_V \sim C_V^{(b)} = AT^{-2/5}$). For low T, on the other hand, $\lambda(T)$ will be large compared to the size R, so that the cavity will be almost frozen. The crossover from an increase to constant gives rise to the peak. Notice we have assumed no particular theory, nor any divergence of $\lambda(T)$ here, only that a very small cavity (relative to λ) is stuck. Hence, the mere presence of this peak does not allow us to discriminate among theoretical frameworks. We need to be more quantitative.

The penetration length λ is conceptually different from the correlation length ξ [20, 22, 37, 38]. The correlation length is a measure of the distance that two points must be separated form each other so that the local state is mutually independent (or in a cavity, how large must the cavity be so that the state at the center is independent from the state at the walls). The penetration length is only meaningful in the presence of domains, and is a measure of the width of the domain walls (in a cavity, how

far from the wall a point must be to be independent from the state outside). ξ can also be thought of as a measure of the size of the domains (or cooperatively rearranging regions), and λ as a measure of the interface width, or the extent of the spatial fluctuations of the walls separating such domains or regions. The lengths can be coincide in simple cases (like the Ising model), but in principle they measure two different phenomena.

There are thus two sides in our finite-size story: a finite size is needed for the ABCs border to have an effect, but the converse is not true: with PBCs, for instance, we can have finite size but no border effects. Hence we must try to include, but separate, both effects: that of the ABCs border (related to λ) and that of the finite size (related to ξ). We believe a reasonable way to do this, at least near the peak, is to write

$$C_V(R,T) = R^{\alpha/\nu}\tilde{c}(y)[1 - f(R/\lambda)]. \tag{1}$$

The factor $R^{\alpha/\nu}\tilde{c}(y)$ is the border-free, FSS form of the specific heat, and it would be a safe bet in most finite-size systems with PBCs [39]. Through the scaling variable $y \equiv R^{1/\nu}(T - T_c)/T_c$, the finite-size term contains all the information about the possible existence of a finite-temperature transition, T_c, and about the correlation length $\xi \sim (T - T_c)^{-\nu}$; hence $\tilde{c}(y)$ is a function of ξ/R. The second factor on the r.h.s. is meant to take care of the border: for large R/λ the border function $f \sim 0$ and the effect of the border is negligible (but not necessarily that of finite size). But we need to be more specific as regards $f(x)$ to test our scaling ansatz Eq. 1, so we make the simplest assumption: that the specific heat is zero exactly at the border and relaxes exponentially to the (finite-size) PBCs value. This results in [20]

$$f(x) = 3\left[x^{-1} - 2x^{-2} + 2x^{-3}(1 - e^{-x})\right], \tag{2}$$

with $x = R/\lambda$.

This form of $f(x)$ is certainly an approximation; to understand its significance we must first make three remarks. First, Eq. 1 is qualitatively different from standard FSS only if λ and ξ are two different length scales, otherwise the effect of the border is a mere decoration of the scaling function and standard FSS remains unchanged. Second, in the critical region, $R \sim \xi$, which follows because the peak position is given by the position y_0 of the maximum of $\tilde{c}(y)$. This follows immediately in the usual FSS case; in the general case the analysis is slightly more complicated (see SM [30]), but it remains true that the peak position and its temperature shift are given by $R^{1/\nu}(T - T_c) \simeq y_0$. Third, (at least in the scenarios we consider), λ diverges at T_c, but not as fast as ξ.

When $R/\lambda \to \infty$, Eq. 2 gives correctly $f \to 0$. When $R/\lambda \to 0$, $f(x)$ tends unphysically to 1, but in the critical region λ is large but $R \sim \xi$, so that $R/\lambda \ll 1$. This means the $R/\lambda \to 0$ limit of $f(R/\lambda)$ is irrelevant in the critical region. Very near T_c though, (which is *outside*
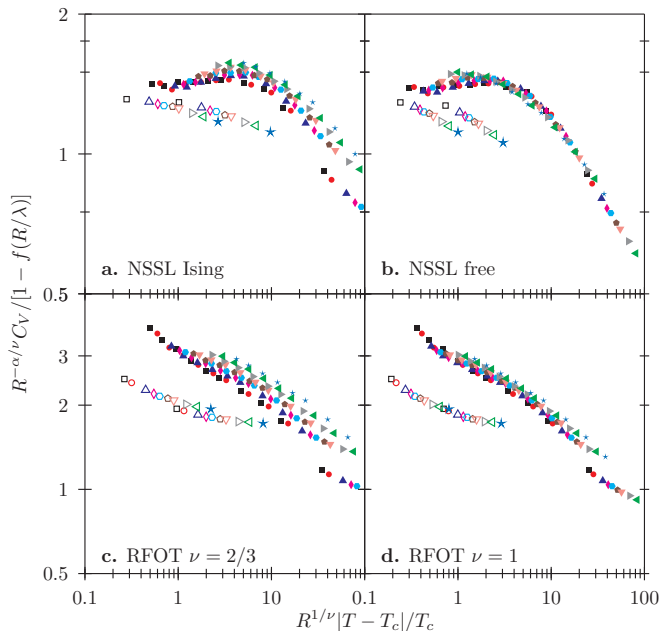
FIG. 2. (color online) Attempts at scaling according to different theoretical scenarios. **a:** NSSL with Ising exponents ($f(x) \equiv 0$, $Tc = 0.17$, $\alpha = 0.11$, $\nu = 0.63$). **b:** NSSL with free exponents ($f(x) \equiv 0$, $Tc = 0.175$, $\alpha = 0.2$, $\nu = 1.0$). **c:** RFOT with $\nu = 2/d$ ($\alpha \equiv 0$, $Tc = 0.17$, $\nu = 2/3$, $f(x)$ as in Eq. 2). **d:** RFOT with $\nu = 1$ ($\alpha \equiv 0$, $Tc = 0.17$, $f(x)$ as in Eq. 2). Colors and symbols indicate different radii (scheme as in Fig. 1), filled symbols are for $T > T_c$, open symbols for $T < T_c$.

the critical region at finite size) our approximation will have the effect of making $\tilde{c}(y)$ divergent as $y \to 0$. Since this unwanted effect can be avoided at the expense of introducing unknown parameters, we have preferred to leave Eq. 2 as is. See SM [30] for a discussion of this point and the possible cure.

Finally, note that in Eq. 1 there are two different mechanisms for the growth of the C_V peak as R increases. When there are no border effects, the $1 - f(R/\lambda)$ factor is absent, and the growth of the peak is controlled by the $R^{\alpha/\nu}$ prefactor [39]. Hence, a nonzero α is normally required to explain a growing (eventually diverging for $R \to \infty$) peak. When there is a border, then the last factor also produces a (moderate) growth of the peak if R grows faster than λ, so that $\alpha = 0$ is compatible with a non-diverging growth of the specific heat for $T \to T_c$.

With this in mind, we now scale our finite-size data according to Eq. 1, namely we try to collapse the data by plotting, $C_V R^{-\alpha/\nu}[1 - f(R/\lambda)]^{-1}$ vs. $R^{1/\nu}(T - T_c)/T_c$. It is clearly useless to attempt to scale with all T_c, ν, α and $\lambda(T)$ free, as there are too many parameters. We will rather try to compare different theoretical scenarios, thus fixing some of these parameters.

Simplest liquid. In the simplest possible physical scenario we have no transition ($T_c = 0$) and only one length

scale, $\lambda \sim \xi$ (i.e. $f \equiv 0$). In this case we are scaling the data as $C_V R^{-\alpha/\nu}$ vs $R^{1/\nu}T$. We then need $\alpha \neq 0$ to account for the growth of the peak. Moreover, it seems reasonable to assume that the standard RG scaling relation (Josephson scaling) $\nu d = 2 - \alpha$ [40] holds in this simplest case. We are therefore left with just one parameter, α. The result is quite bad and no reasonable collapse is obtained for any value of α (not shown).

Not-so-simple liquid (NSSL). What really seems to resist the scaling of the data in the simplest case is the assumption $T_c = 0$. We therefore relax this hypothesis, assuming that a standard phase transition exists at a finite temperature (standard meaning there is only one length scale, so that $\lambda \sim \xi$, and normal FSS ($f \equiv 0$) applies). One such case is that invoked by Tanaka et al. [6], with Ising-like critical exponents (which thus satisfy the relation $\nu d = 2 - \alpha$). This proposal does not achieve a reasonable collapse, irrespective of the value of T_c (Fig. 2a). Fernández et al. [15] have studied the specific heat of our same system under PBCs and seemed to find a divergence at temperature $T_c = 0.195$, with $\alpha = 0.9$. With these values, however, we fail to obtain a collapse (violating Josephson scaling does not help much either). If, however we leave *all three* parameters α, ν and T_c free, we get a reasonable collapse for the data above T_c (Fig. 2b).

Mosaic liquid. Now we assume that the penetration length, λ, and correlation length, ξ, grow differently. The increase of the peak for increasing R implies that $\lambda \ll \xi$. This is the only case in which ABCs really have some nontrivial qualitative effect, because this is the only way in which we can achieve a growth of the peak with $\alpha = 0$: in this case, the specific heat has a kink in the bulk limit, rather than a divergence. This is exactly what is supposed to happen in the random first-order theory (RFOT), as well as in some mean-field spin-glass models, in particular the p-spin [18, 41–43]. The RFOT transition is first order in the sense that it has a discontinuous order parameter, but second order in the Ehrenfest sense [42, 43]. Quite generally $\alpha = 0$ in RFOT, as a consequence of the fact that the configurational entropy vanishes at T_c, giving a discontinuity of the derivative of the total entropy at the transition [42–44]. There is theoretical [38] as well as numerical [20, 22] evidence that within the RFOT scenario indeed penetration and correlation length are different things and that $\lambda \ll \xi$.

In this scenario both ξ and λ diverge at T_c, but with different critical exponents. For $\lambda(T)$, the prediction is that $\lambda \sim |T - T_c|^{-1/2}$ in three dimensions [38]. The exponent ruling the ξ divergence is $\nu = 1/(d - \theta)$ [45], where θ is the stiffness exponent, for which different values have been predicted. Some approximations [45] give $\theta = d/2$, corresponding to $\nu = 2/d$, while others [22, 46] give $\theta = d - 1$, which yields instead $\nu = 1$. In three dimensions, both predictions imply $\nu > 1/2$ and thus $\xi \gg \lambda$ near T_c.

To perform the $\lambda \neq \xi$ scaling we need to plot $C_V R^{-\alpha/\nu}[1 - f(\lambda/R)]^{-1}$ vs. $R^{1/\nu}(T - T_c)/T_c$. We use Eq. 2 as an approximation for $f(x)$, but we need also $\lambda(T)$. For this we have taken the data of ref. [20] and fitted them to a power law $a|T - T_c|^{1/2}$ [38], leaving a as fitting parameter but fixing T_c self-consistently to the value that gives the best collapse of C_V. The resulting scalings are shown in Fig. 2 (panels c and d). Both have $\alpha = 0$ in accordance to RFOT predictions, with $\lambda(T)$ for $T > T_c$ taken from the power law fit as explained above. T_c is a free parameter, while ν is fixed to the values 2/3 and 1 according to the different predictions. The RFOT scaling with $\nu = 2/3$ (Fig. 2c) does not give a good collapse of the data, while using $\nu = 1$ does a rather good job (Fig. 2d) for $T > T_c$. For $T < T_c$ we do not have data to fit $\lambda(T)$, hence we have used the same power law with a prefactor a' chosen to give the best collapse. So the $T < T_c$ branch has a better-looking collapse but with two free parameters instead of one.

Though ABCs differ from more usual BCs such as PBCs in that they bring forward the existence of two lengthscales, the critical temperature and exponents are independent of the boundary conditions, since in the $R \to \infty$ limit all observables are independent of the boundary conditions [47] unless control parameters are such that the system is below a thermodynamic transition [48]. It is not possible to perform the same analysis under PBCs in this system, because systems very small or below $T \approx 0.2$ crystallize before C_V can be measured. The values we have been able to obtain are compatible with the NSSL scaling (Fig. 3c), but also with other values (see SM [30] for more details). It is not possible to collapse the PBCs data using Eqs. 1 and 2, since $f(x)$ is constructed specifically for cavities (i.e. frozen boundaries). We do not delve into how the existence of two lengthscales as proposed by RFOT should manifest itself under PBCs; we merely point out that these data do not contradict a scaling with a nonzero critical temperature.

Finally, we have tried a different BC on a cavity, repeating the analysis with random boundary conditions (RBCs). RBCs are the same as ABCs except that the outer (fixed) particles are at random positions. Fig. 3 shows the result of applying the two most successful scalings to the RBCs data. *This figure introduces no new parameters:* RBCs data are scaled using the same T_c, $\lambda(T)$ and exponents adjusted for the ABCs case. Above T_c both sets of data can be scaled with the same parameters, and, at least under RFOT, with the same scaling function. Below T_c (open symbols), the scaling function seems to depend on the boundaries; we note in particular that the RBCs data can be scaled in the RFOT scenario without adjusting the prefactor of the $\lambda(T)$ power law.

In summary, we have studied spherical cavities with amorphous and random BCs. Together with swap MC that can equilibrate small cavities, this has allowed us to do a FSS analysis of the specific heat, which is impossible
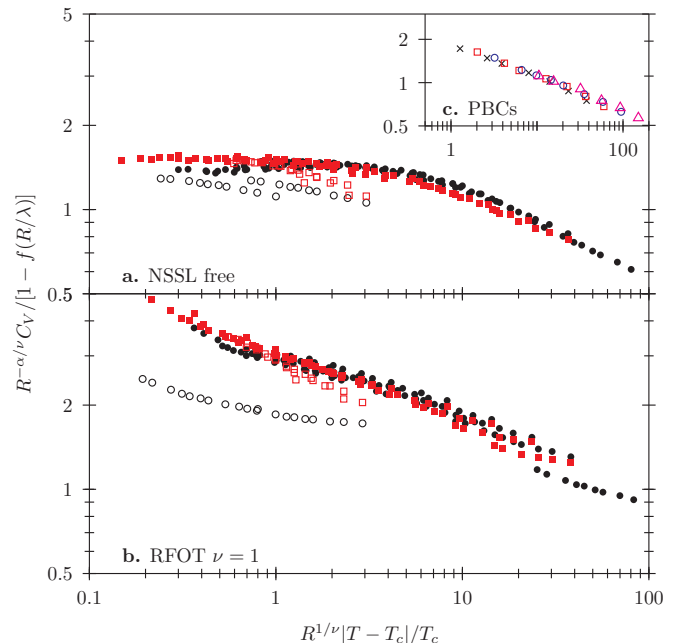

FIG. 3. Scaling plots for C_V data under random boundary conditions (RBCs) (red squares) and amorphous boundary conditions (ABCs) (black circles) according to the NSSL (panel a) and RFOT (panel b) scenarios. T_c, α, ν and $\lambda(T)$ are the same for both sets of data and are those adjusted for ABCs and quoted in Fig. 2. The only difference is that in the RFOT case, we have set $a' = a$ in the $\lambda(T)$ expression to scale RBCs data. Panel c: PBCs data for cubic systems of side $L = 8$ (black crosses), 12.7 (red squares), 20.16 (blue circles), and 32 (purple triangles), scaled with the same exponents and T_c of the NSSL case (panel a).

under PBCs due to crystallization. We have found a peak in C_V, which can be scaled under two different scenarios, NSSL and RFOT. The first implies a divergence of C_V in the thermodynamic limit, while the second predicts a discontinuity. Both are of comparable quality, but NSSL has three free parameters, compared to one (two below T_c) for RFOT. Within RFOT, only $\nu = 1$ gives a reasonable collapse, suggesting a stiffness exponent $\theta = d - 1$.

We finally emphasize that in all cases our collapse attempts *yield a finite T_c*, of around 0.17. This means that the peak survives the thermodynamic limit. Since in this limit observables must be independent of the boundary conditions (unless there is phase coexistence [47]), this result implies the existence of an anomaly or phase transition in the $R \to \infty$ limit, independently of the particular BCs we have employed. Investigation of more realistic and better glassforming liquids is needed. This will be a challenge, as swap MC is unsuitable for most systems. Nevertheless, these results seem a strong support for thermodynamic theories of the glass transition.

---

* Present address: Instituto de Física de Líquidos y Sistemas Biológicos (IFLYSIB), c.c. 565, 1900 La Plata, Argentina

[1] C. A. Angell, Science **267**, 1924 (1995).

[2] L. Berthier and G. Biroli, Rev. Mod. Phys. **83**, 587 (2011).

[3] G. Biroli, J.-P. Bouchaud, A. Cavagna, T. S. Grigera, and P. Verrocchio, Nature Phys. **4**, 771 (2008).

[4] A. Widmer-Cooper, H. Perry, P. Harrowell, and D. R. Reichman, Nature Phys. **4**, 711 (2008).

[5] E. Lerner, I. Procaccia, and J. Zylberg, Physical Review Letters **102**, 125701 (2009).

[6] H. Tanaka, T. Kawasaki, H. Shintani, and K. Watanabe, Nature Mater **9**, 324 (2010).

[7] F. Sausset and D. Levine, Phys. Rev. Lett. **107**, 045501 (2011).

[8] D. Coslovich, Phys. Rev. E **83**, 051505 (2011).

[9] B. Charbonneau, P. Charbonneau, and G. Tarjus, Phys. Rev. Lett. **108**, 035701 (2012).

[10] G. M. Hocky, T. E. Markland, and D. R. Reichman, Phys. Rev. Lett. **108**, 225506 (2012).

[11] W. Kob, S. Roldán-Vargas, and L. Berthier, Nat. Phys. **8**, 164 (2012).

[12] M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).

[13] H. Sillescu, J. Non-Cryst. Sol. **243**, 81 (1999).

[14] J. Kurchan and D. Levine, J. Phys. A: Math. Theor. **44**, 035001 (2011).

[15] L. A. Fernández, V. Martín-Mayor, and P. Verrocchio, Phys. Rev. E **73**, 020501 (2006).

[16] S. Karmakar, C. Dasgupta, and S. Sastry, Proc. Natl. Acad. Sci. USA **106**, 3675 (2009).

[17] A. Montanari and G. Semerjian, J. Stat. Phys. **125**, 23 (2006).

[18] J.-P. Bouchaud and G. Biroli, J. Chem. Phys. **121**, 7347 (2004).

[19] R. L. Jack and J. P. Garrahan, J. Chem. Phys. **123**, 164508 (2005).

[20] A. Cavagna, T. S. Grigera, and P. Verrocchio, Phys. Rev. Lett. **98**, 187801 (2007).

[21] L. Berthier and W. Kob, Phys. Rev. E **85**, 011102 (2012).

[22] G. Gradenigo, R. Trozzo, A. Cavagna, T. S. Grigera, and P. Verrocchio, J.Chem. Phys. **138**, 12A509 (2013).

[23] S. Karmakar and G. Parisi, Proc. Natl. Acad. Sci. **110**, 2752 (2013), http://www.pnas.org/content/110/8/2752.full.pdf+html.

[24] Notice that one-time thermodynamic quantities, like energy, density or magnetization, are not sensitive to ABCs [27, 37, 49], while correlation functions and susceptibilities may be.

[25] T. S. Grigera and G. Parisi, Phys. Rev. E **63**, 045102 (2001).

[26] B. Bernu, J. P. Hansen, Y. Hiwatari, and G. Pastore, Phys. Rev. A **36**, 4891 (1987).

[27] A. Cavagna, T. S. Grigera, and P. Verrocchio, J. Stat. Mech. **2010**, P10001 (2010).

[28] H. Tanaka, Eur. Phys. J. E **35**, 113 (2012).

[29] A. Cavagna, T. S. Grigera, and P. Verrocchio, J. Chem. Phys. **136**, 204502 (2012).

[30] See Supplemental Material [url], which includes Refs. [31, 32].

[31] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983).

[32] J. R. Errington, P. G. Debenedetti, and S. Torquato, J. Chem. Phys. **118**, 2256 (2003).

[33] Y. Rosenfeld and P. Tarazona, Mol. Phys. **95**, 141 (1998).

[34] T. S. Ingebrigtsen, A. A. Veldhorst, T. B. Schrøder, and J. C. Dyre, J. Chem. Phys. **139**, 171101 (2013).

[35] D. Bolmatov, V. V. Brazhkin, and K. Trachenko, Sci. Rep. **2**, 421 (2012).

[36] Q. Yan and T. S. Jain and J. J. de Pablo , Phys. Rev. Lett. **92**, 235701 (2004).

[37] E. Zarinelli and S. Franz, J. Stat. Mech. **2010**, P04008 (2010).

[38] G. Biroli and C. Cammarota, "Fluctuations and shape of cooperatively rearranging regions in glass-forming liquids," arXiv: 1411.4566 (2014).

[39] M. E. J. Newman and G. Barkema, *Monte Carlo Methods in Statistical Physics* (Oxford University Press, Oxford, 1999).

[40] J. J. Binney, N. J. Dowrick, A. J. Fisher, and M. E. J. Newman, *The theory of critical phenomena* (Oxford University press, 1992).

[41] T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. **58**, 2091 (1987).

[42] A. Crisanti and H.-J. Sommers, Z. Phys. B **87**, 341 (1992).

[43] B. Coluzzi, M. Mezard, G. Parisi, and P. Verrocchio, J. Chem. Phys. **111**, 9039 (1999).

[44] V. Lubchenko and P. G. Wolynes, Ann. Rev. Phys. Chem. **58**, 235 (2007).

[45] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A **40**, 1045 (1989).

[46] S. Franz, J. Stat. Mech. **2005**, P04001 (2005).

[47] It is understood that crystalline boundaries are excluded. This is necessary to remain in the supercooled liquid (a crystalline border would make the whole cavity crystallize). We mean independent from different BCs (such as ABCs, PBCs or RBCs) within the (metastable)liquid phase. See SM for a more complete discussion.

[48] G. Parisi, *Statistical Field Theory* (Westview Press, 1998).

[49] V. Krakoviack, Phys. Rev. E **82**, 061501 (2010).