Response to “Comment on ‘Static correlations functions and domain walls in glass-forming liquids: The case of a sandwich geometry’” [J. Chem. Phys. 144, 227101 (2016)]

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The point-to-set correlation function has proved to be a very valuable tool to probe structural correlations in disordered systems, but more than that, its detailed behavior has been used to try to draw information on the mechanisms leading to glassy behavior in supercooled liquids. For this reason it is of primary importance to discern which of those details are peculiar to glassy systems, and which are general features of confinement. Thus the concerns raised in Ref. 1 definitely need to meet an answer.

The Comment proposes an alternative analysis of the numerical data presented in Ref. 2, according to which the behaviour of the point-to-set correlation function can be interpreted as a linear superposition of boundary effects, rather than the effect of non-trivial thermodynamics. We believe this alternative explanation is not compelling. The problem is that the expression Eq. (1) of Ref. 1 for the correlation $\rho_{la}(x,y)$, where $\rho_{la}(x,y)$ is the linear superposition of the influence of the two boundaries, is based on the assumption that at least one of the two points $x$ or $y$ is “far enough” from an amorphous boundary. According to the Comment, Eq. (1) suggests the general validity of a superposition principle for the data of Ref. 2. What is puzzling is that the most relevant information on non-trivial thermodynamics contained in Ref. 2 is related to narrow sandwiches, which is precisely the case where Eq. (1) does not apply. Therefore, since Eq. (1) only suggests the validity of a superposition principle and in practice does not apply to the most important situation, i.e., narrow sandwiches, it seems to us that there is no theory of simple liquids behind the superposition principle, but just the assumption of a reasonable physical mechanism. We find therefore quite unconvincing the statement according to which Eq. (1) is the “simple result” previously not available which allowed to “make concrete” the superposition scenario brought forward in Ref. 1. Hence, the Comment provides an explanation of the non-exponentiality of the point-to-set correlation function in the context of the 1D Ising model. Let us remark to this purpose that there are several critical phenomena taking place in simple liquids, like the demixing transition in a binary mixture or the liquid-vapour transition in a monodisperse system, which have universal features well captured by the physics of the Ising model. Moreover, even some general ideas about the random first-order transition theory (RFOT), for instance, how the point-to-set correlation should behave changing the size of the confining cavity in a system with short-range interactions, can be put under scrutiny looking at the corresponding behaviour in magnetic systems, see, for instance, Ref. 3 but also Sec. VI of Ref. 2. At the same time we need to warn the reader that such a specific problem, as whether the behaviour of the point-to-set correlation function for a 1D glass-forming liquid is due to trivial finite-size effects or to thermodynamic anomalies, cannot be solved in favour of a “simple liquid scenario” just looking at the behaviour of a 1D Ising model: the latter shares too few commonalities with the system of interest from the viewpoint of such a specific question. For instance, any representation of a fluid in terms of an Ising model cannot distinguish between a simple fluid and a fluid with a complex energy landscape. The “simple liquid scenario” cannot be supported solely by the results on the 1D Ising in particular due the lack of any other favourable evidence: we remark that the only theoretical formula related to simple liquids (Eq. (1) of the Comment) does not hold in the regime of narrow slits.

Apart from this inconsistency, we would like to point out that results more recent than Ref. 2 provide clear evidence that non-trivial thermodynamic behaviour occurs in a confined supercooled liquid. Not only theoretical models show that confinement, irrespectively to the kind of boundary conditions,4,5 is already sufficient to originate thermodynamic anomalies, but numerical evidence independent from the behaviour of the point-to-set correlation function clearly support the idea that these thermodynamic anomalies are effectively present in the behaviour of confined supercooled liquids.6,7 Support for the existence of a point-to-set correlation length $\xi_{PS}$ has also been found from the peak of the specific heat of a confined supercooled liquid as a function of the cavity size,6 as well as from the distribution of the overlap as a function of the cavity size,7 which at $\xi_{PS}$ is bimodal.

In conclusion, considering all the numerical and theoretical information about the behaviour of supercooled liquids in confined geometries gathered in recent years, it
seems to us that the RFOT theory scenario remains still the most compelling explanation of the non-exponential decay of the point-to-set correlation function first discovered in Ref. 8.