On the critical behavior of the specific heat in glass-formers

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The glass-transition differs from standard phase transitions in that the equilibration time of glass-formers (polymers, supercooled liquids, colloids, granulars, super-conductors, ...) diverges without apparent dramatic changes in their structural properties. Reconciling these two faces is a major challenge for condensed matter physics.

A general mechanism producing a divergence of the equilibration time of an homogeneous system at finite temperature is the divergence of a correlation length (*critical slowing down*). Since static quantities do not seem to reveal fluctuations over large length scales close to the glass-transition, it has been suggested that dynamic functions, such as time-correlators, must be rather studied (*dynamic heterogeneities* scenario).

Here we report numeric simulations at odds with the previous scenario. Exploiting a fast Monte-Carlo algorithm which reduces of a factor ~ 200 the relaxation time, we find in a fragile glass-forming liquid large scale fluctuations of the specific heat, a static function[1]. Moreover, the infinite-volume specific heat shows a power-law divergence. This suggests that the dynamical features of the glass-transition might be ascribed to critical slowing down arising from a continuous phase transition. The difficulty in recognizing it is due to the fact that standard experiments are not devised to detect spatial fluctuations in the energy density.

A large correlation-length can be detected through Finite-Size effects. In Fig. 1(a) we show the specific heat dependence on the size of the simulation box, L. Down to $T = 0.921T_{\rm mc}$ ($T_{\rm mc}$ being the mode-coupling temperature) no finite-size effects are detected. However, for $T = 0.897T_{\rm mc}$, a noticeable growth of the specific-heat is found up to $L \sim 4$nm, which is then a rough estimate of the correlation-lenght. This length is well above the interaction range (a fews $\mathring{A}$). Consistently, Fig. 1(b) shows that at $T = 0.897T_{\rm mc}$ the time-correlator of the energy decays more slowly as L grows. Studying the critical behavior in the infinite-volume specific heat (Fig.1(c)) is difficult due to the presence of a large non-critical background. Fortunately, the background is described by the Rosenfeld-Tarazona law, $T^2 C_{\rm V} \propto T^{8/5}$. From $T \sim T_{\rm mc}$ to beyond $10T_{\rm mc}$ the $T^{8/5}$ law is extremely accurate (Fig.1(c)), while at lower temperatures *deviations* start to be significant. Such deviations point toward the existence of a critical point, since they show a power-law divergence over two decades (Fig.1(d)).

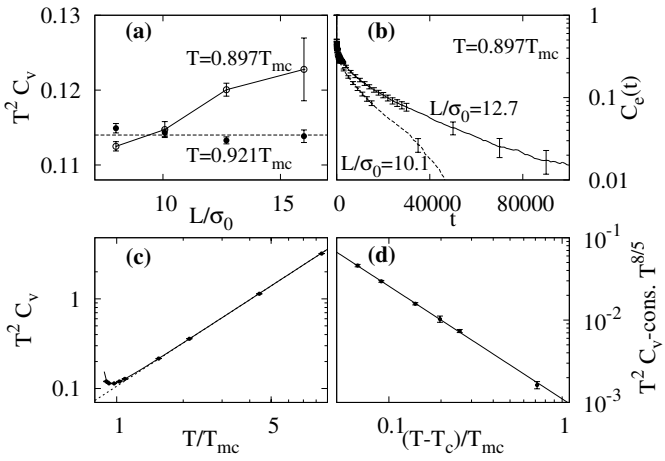

Figure 1: Panel (a): the specific heat is a growing function of the simulation box size, until the system becomes much larger than the correlation length. This is visible for $L < 12\sigma_0$ ($\sigma_0 = 3.5\mathring{A}$ in Argon units) at $T = 0.897T_{\rm mc}$, but not at $T = 0.921T_{\rm mc}$. The correlation length grows quickly close to $T_{\rm c}$, which is confirmed by the time correlator for the potential energy (b). Panel (c): infinite volume specific-heat vs. temperature. The dotted line is the $T^{8/5}$ Rosenfeld-Tarazona law. Deviations from the $T^{8/5}$ law can be fitted by a critical divergence (full line in (d)).

From our simulations potential energy, rather than density, fluctuations emerge as the best candidates for the study of this critical phenomenon. While measurements of the frequency dependence of the specific heat are an appealing possibility to estimate the energy relaxation time, the correlation-length could be studied by Finite-Size Scaling of the specific-heat and of relaxation times in films or in larger pores than previously used to confine glass-formers.

References

[1] L.A. Fernandez, V. Martin-Mayor, P. Verrocchio, cond-mat/0504327