Evidence for a spinodal limit of amorphous excitations in glassy systems

LETTER

Evidence for a spinodal limit of amorphous excitations in glassy systems

C Cammarota[1,2]**, A Cavagna**[2,3]**, G Gradenigo**[4,5]**, T S Grigera**[6,7] **and P Verrocchio**[4,5,8]

[1] Dipartimento di Fisica, Università di Roma 'Sapienza', Piazzale Aldo Moro 5, 00185, Roma, Italy
[2] Center for Statistical Mechanics and Complexity (SMC), CNR-INFM, Italy
[3] Istituto Sistemi Complessi (ISC), CNR, Via dei Taurini 19, 00185 Roma, Italy
[4] Dipartimento di Fisica, Università di Trento, via Sommarive 14, 38050 Povo, Trento, Italy
[5] INFM CRS-SOFT, c/o Università di Roma 'Sapienza', 00185, Roma, Italy
[6] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA) and Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal 4, 1900 La Plata, Argentina
[7] CCT La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina
[8] Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), Spain
E-mail: chiara.cammarota@roma1.infn.it, andrea.cavagna@roma1.infn.it, gradenigo@science.unitn.it, tgrigera@gmail.com and paolo.verrocchio@unitn.it

Abstract. What is the origin of the sharp slowdown displayed by glassy systems? Physical common sense suggests there must be a concomitant growing correlation length, but finding this length has been nontrivial. In random first-order theory, it is given by the size of amorphous excitations, which depends on a balance between their mutual interfacial energy and their configurational entropy. But how these excitations disappear when crossing over to the normal high temperature phase is unclear, chiefly due to lack of data about the surface tension. We measure the energy cost for creating amorphous excitations in a model glass-former, and discover that the surface tension vanishes at a well-defined spinodal energy, above which amorphous excitations cannot be sustained. This spinodal therefore marks the true onset of glassiness.

It is only recently that a *static* growing correlation length ξ has been clearly detected in glass-forming liquids [1, 2], by measuring a point-to-set correlation function [3, 4]. The idea is the following: consider a liquid region of size R subject to amorphous boundary conditions provided by the surrounding liquid frozen into an equilibrium configuration. The external particles act as a pinning field favoring internal configurations which best match the frozen exterior. Clearly, the effect of the border on the innermost part of the region becomes smaller as R grows larger. Less trivially, on lowering the temperature the effect of the amorphous boundary conditions propagates deeper into the region. More precisely, if we measure some correlation (or overlap) $q_c(R)$ between the initial configuration of the region and that reached at infinite time under the effect of the amorphous boundary conditions, the decay of $q_c(R)$ is slower with lower T [1, 2], which shows the existence of an increasing static correlation length ξ. $q_c(R)$ is the point-to-set correlation function. Interestingly it displays a strongly non-exponential decay at low temperature, which is a unique thermodynamic landmark of the deeply supercooled phase [2] and finds an explanation in the context of random first-order theory (RFOT).

According to RFOT, the decay of $q_c(R)$ is regulated by the competition between a surface energy cost, YR^θ, tending to keep the region to the same amorphous state as the external configuration, and a configurational entropy gain, $T\Sigma R^d$, favoring a transition to another of the exponentially many metastable amorphous states, $\mathcal{N}(R) \sim \exp(R^d\Sigma)$, available to the region [5]. The cost/gain terms balance at $R = \xi \equiv (Y/T\Sigma)^{1/(d-\theta)}$: for $R < \xi$ the surface cost $Y_c R^\theta$ keeps the region in the same state as the external environment; for $R > \xi$ the entropic gain $T\Sigma R^d$ dominates and the region is free to rearrange. RFOT therefore identifies the scale of the decay of $q_c(R)$ with the typical size ξ of the rearranging regions, and this is the static correlation length. Note that ξ is also the largest scale over which it is sensible to define a metastable state: a state defined over a region much larger than ξ is unstable against fragmentation into amorphous excitations of typical scale ξ.

The existence of many amorphous excitations is central to the mechanism of relaxation of RFOT. But for such nontrivial excitations to exist, a nonzero surface tension is necessarily required. Moreover, the regime of validity of RFOT is bounded by a spinodal mechanism. While at mean-field level the spinodal transition corresponds to the point where metastable states disappear [6], RFOT predicts that it is instead the surface tension Y between finite dimensional amorphous excitations that vanishes at temperatures higher than some spinodal value [7], loosely identified with the mode coupling temperature [8]. The aim of this work is to measure the surface tension between amorphous excitations and to test the validity of the spinodal scenario. We expect however that such a scenario may become very sharp only when choosing energy rather than temperature as the control parameter. We will show that, with this choice, a spinodal transition is indeed present.

The determination of the surface free energy, between the amorphous excitations, is very challenging, first, because the interfaces are hard to detect, and second, because their lifetime is necessarily finite. Excitations are constantly forming and relaxing: this is the relaxation mechanism of RFOT, through which the whole liquid state is slowly explored. The study of the time evolution of the surface tension of artificially created excitations within equilibrium configurations allows one to gain some physical insights about the relation between the free energy needed to create them and their shape [9]. As a drawback, one needs to introduce the lifetime of such excitations as an extra parameter. This time dependence of the results makes the analysis quite onerous. Here we focus instead on the

surface tension of inherent structures (ISs), i.e. local minima of the potential energy [10]. Although the IS approach measures internal energy rather than free energy, and though the numerical value of the surface tension may change due to the approximation, the existence of the putative spinodal point should not depend on the fact that we discard entropy. The big advantage of ISs is the possibility of defining a control parameter appropriate for studying a spinodal that would otherwise be very hard to detect. We expect in fact that temperature will not fundamentally change this picture, but merely blur it. Moreover, we shall show that the spinodal point is very close to the *threshold* energy below which minima start to dominate the energy landscape [11, 12]. Thus within the range of energies under study here the ISs approximate well enough the thermal configurations. In systems with a non-analytic potential such as hard spheres an inherent structure corresponds to a collectively jammed configuration, and different strategies for computing their properties have been proposed (see for example [13]). In this case, density instead of energy would be the control parameter.

We consider a set of ISs obtained by minimizing equilibrated instantaneous configurations of a model soft-sphere glass-former[9]. Our lowest working temperature is $T = 0.89\,T_{\rm c}$ ($T_{\rm c}$ is the mode coupling temperature [8]). Given a pair α and β of ISs, we exchange between them all particles located within a sphere of radius R. We then minimize the two configurations thus obtained to produce two new ISs. Each of them is a hybrid minimum, resembling the *parent* minima far from the surface of the sphere but rearranged close to it (figure 1). Note that the hybrid configuration is nevertheless a typical IS of the system: the only reason that we are able to visualize the interface is that we know *a priori* the shape and position of the excitation and we can use the parent configurations as references for calculating the overlap.

For each hybrid IS we compute the surface energy $E^{\rm s}_{\alpha\beta}$ as $E^{\rm s}_{\alpha\beta} = E_{\alpha\beta} - E^{\rm int}_{\beta} - E^{\rm ext}_{\alpha}$, with the parent IS contribution $E^{\rm ext/int} = \sum_{i,j:|\mathbf{r}_i|\gtrless R} v_{ij}(\mathbf{r}_i - \mathbf{r}_j)$. Figure 2 shows the sample-averaged surface energy, $E^{\rm s}$, versus R for several temperatures. There is a well-defined relationship between surface energy and size, regulated by the temperature: at fixed R, $E^{\rm s}$ increases with decreasing T. The data do not correspond to a single power-law scaling, so we propose

$$E^{\rm s} = Y_\infty R^\theta - \delta R^\omega, \tag{1}$$

where Y_∞ is the asymptotic surface tension and $\omega < \theta$. The sub-leading δR^ω correction is quite natural. It is present in liquids (with $\omega = 1$) due to curvature effects [14], and in disordered systems, where it may arise either from bulk contributions, as in the random

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[9] The system is a 3D soft-sphere binary mixture [21]. Particles are of unit mass and belong to one of two species $\mu = 1, 2$, present in equal amounts and interacting via a potential

$$V = \sum_{i>j}^{N} v_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i>j}^{N} \left[\frac{\sigma_{\mu(i)} + \sigma_{\mu(j)}}{|\mathbf{r}_i - \mathbf{r}_j|} \right]^{12},$$

where the radii σ_μ are fixed by the conditions $\sigma_2/\sigma_1 = 1.2$, $(2\sigma_1)^3 + 2(\sigma_1 + \sigma_2)^3 + (2\sigma_2)^3 = 4\ell_0^3$, and ℓ_0 is the unit of length. The particle density is $\rho = N/V = l_0^{-3}$. A smooth long-range cut-off is imposed by setting $v_{ij}(r) = B_{ij}(a-r)^3 + C_{ij}$ for $r > r_{\rm c} = \sqrt{3}$ and $v_{ij}(r) = C_{ij}$ for $r > a$, where a, B_{ij}, and C_{ij} are fixed by requiring continuity up to the second derivative of $v_{ij}(r)$. Temperature is measured in units of energy. Simulations were done with a Metropolis Monte Carlo method with particle swaps [22]. The mode coupling temperature $T_{\rm c}$ for this system is $T_{\rm c} = 0.226$ [23]. $N = 16384$ particles were considered in a box of length 25.4. Minimization of instantaneous configurations was done with the LBFGS algorithm [24].
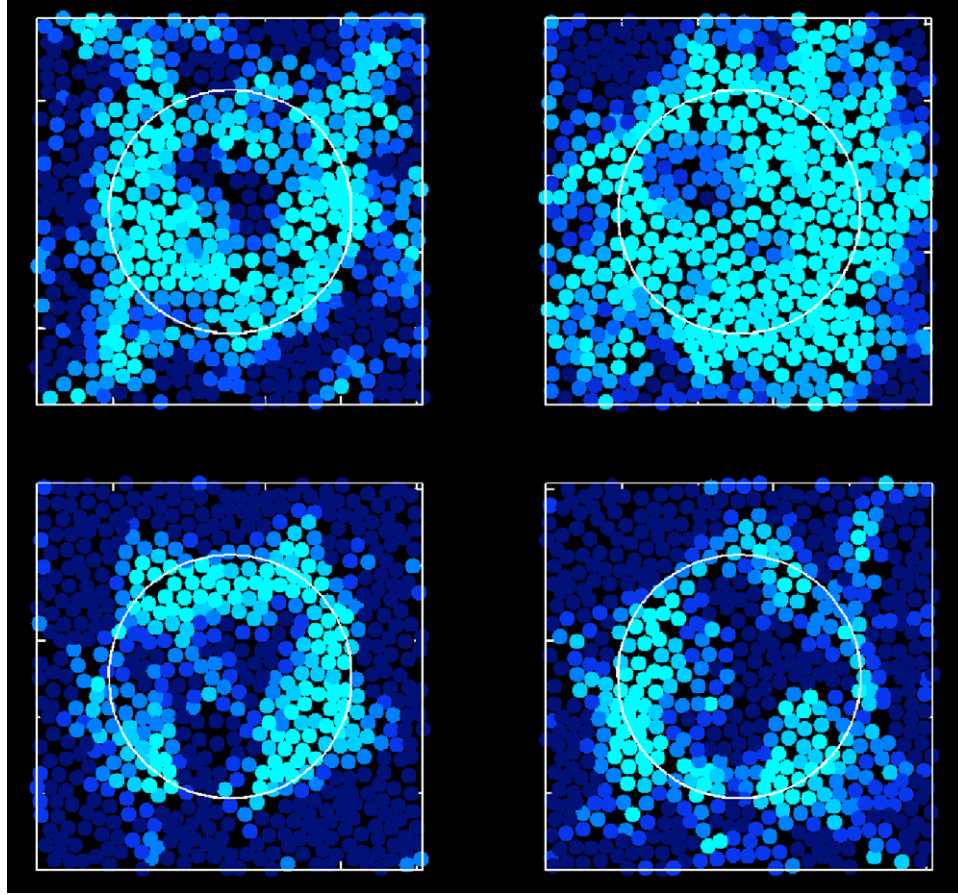
Figure 1. Overlap between the configuration right after the exchange of the spheres and the hybrid inherent structure after minimization. Only a thin slice located at half the height of the 3D system is shown. Colors code for the displacement of the particle after the artificial excitation was created (dark blue: small displacement, high overlap; light blue: large displacement, small overlap). Upper panel: two configurations at high temperature $T = 1.33\,T_{\rm c}$. Lower panel: two configurations at low temperature $T = 0.89\,T_{\rm c}$. The hybrid minimum clearly bears memory (high overlap, dark blue) of the parent ISs far from the boundary of the sphere (white circle). On the other hand, particles move the along the interface (low overlap, light blue).

field Ising model [15], or from interface roughening that lowers the surface energy, as in the random bond Ising model [16].

We must choose the exponents of equation (1) with some criterion, because the nonlinear fit with four parameters is marginally stable, and many sets of parameters give good fits. Our data strongly suggest the conservative choice $\theta = 2$, which seems to describe the large R behavior better than the alternative $\theta = 3/2$ predicted by a wetting argument [17, 18]. The value $\theta = 2$ is also found in spin models with finite range interactions [19]. To fix ω, we take equation (1) as valid for the whole population of surface energies (instead of just the average), and ascribe all fluctuations of $E_{\alpha\beta}^{\rm s}$ the quantity

$$\delta_{\alpha\beta} = \frac{Y_\infty R^2 - E_{\alpha\beta}^{\rm s}}{R^\omega}.$$
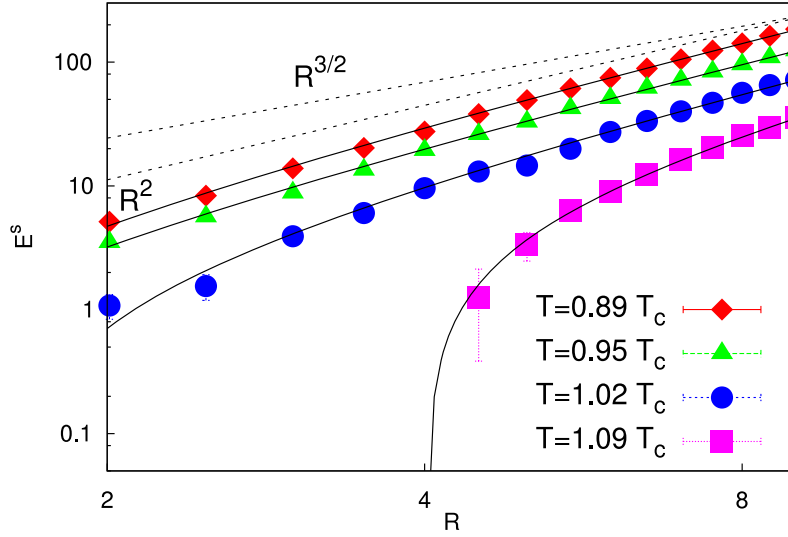
(2)

Figure 2. E^{s} versus excitation radius R at various temperatures. Full lines are fits using equation (1), with $\theta = 2$ and $\omega = 1.5$. Dotted lines show the power laws with exponents 2 and 3/2 for reference. Error bars are smaller than symbol size.

We then fix ω at the value which makes the variance $\text{Var}[\delta(\omega)]$ independent of R. This is a typical behavior in disordered media [15, 16, 20] and finds some confirmation here from the violation of the central limit theorem shown by the variance of $Y_{\alpha\beta}$ at large R (see figure 5, inset). This procedure gives $\omega = 1.5(2)$.

With θ and ω thus fixed, equation (1) fits the $E^{\text{s}}(R)$ data very well (figure 2), and we obtain the asymptotic surface tension Y_{∞} as a function of the temperature T (figure 3, top). We find that Y_{∞} decreases for increasing T, and becomes quite small above T_{c}. This behavior makes sense, indicating that amorphous excitations become softer as the temperature is raised. This is indeed what we expect physically as the system moves towards a spinodal point. Yet, the decrease of the surface tension is rather smooth, so it is hard to sharply define a spinodal temperature. Since T_{c} roughly corresponds to the point where activated processes become important for the relaxation of the system, one might expect the spinodal and T_{c} to coincide [7]. However, our numeric data show that this is not really the case: even though T_{c} is definitely within the range of temperatures where Y_{∞} is becoming negligible, amorphous excitations with nonzero surface tension exist even above T_{c}. On the other hand, the onset of glassiness is *never* sharp in temperature. However, taking energy rather than temperature as a control parameter, a well-defined spinodal point clearly emerges: the Y_{∞} versus $e_{\text{IS}}(T)$ curve is nearly linear (figure 4, left), and Y_{∞} vanishes at an energy e_{th}.

It is quite interesting to note that e_{th} is very close to the *threshold* energy, i.e. the value below which minima start to dominate the energy landscape [11, 12]. More precisely, the threshold is defined as the point where the instability index of saddles vanishes (figure 4, right). Hence, the true spinodal point of amorphous excitations, fixing the upper limit of stability of the RFOT mechanism, is the very same energy e_{th} where a topological transition from saddle to minima takes place. This sharp transition in phase space,
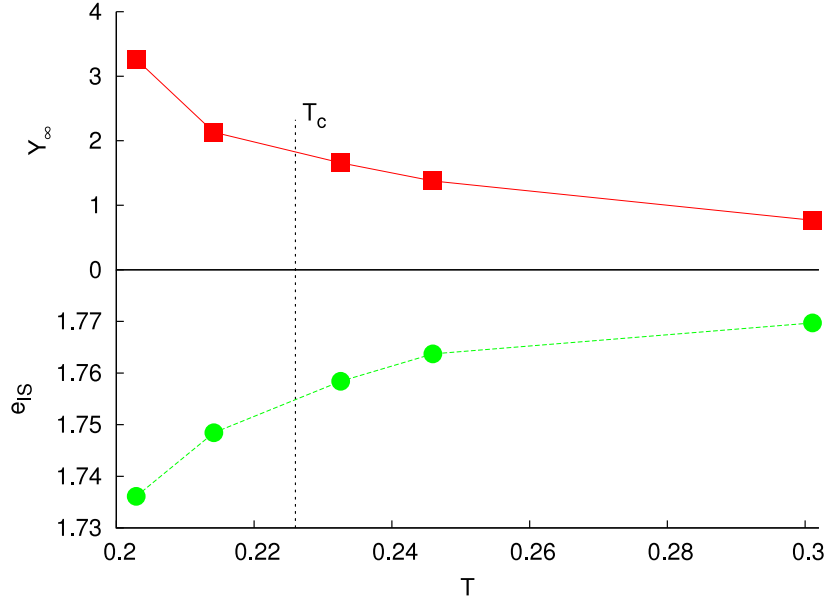
Figure 3. Upper panel: Y_∞ as a function of the quenching temperature of the inherent structures. The vertical dotted line marks the mode coupling temperature. The surface tension decreases on increasing T, although too smoothly to indicate a sharp spinodal temperature. Lower panel: inherent structure energy as a function of the quenching temperature.

namely the vanishing of the saddle index from above and of the surface tension from below, becomes a smooth crossover when studied as a function of temperature. Our result therefore indicates that energy, and not temperature, is the control parameter of the glass transition and that e_{th} truly marks the onset of glassiness: below the threshold energy unstable saddles give way to stable minima, and a nonzero surface tension develops, making it possible to sustain local amorphous excitations, whose relaxation is responsible for the sharp increase of the relaxation time.

We next compute the distribution of the single-sample surface tension,

$$Y_{\alpha\beta} \equiv \frac{E_{\alpha\beta}^{\text{s}}}{R^2}. \tag{3}$$

Numerical results [1] are inconsistent with the original version of RFOT, which assumes a single value of Y for all pairs of amorphous excitations, so a generalized RFOT has been proposed which assumes the existence of a broad distribution of Y [2] when considering different pairs of ISs. The distribution $P(Y, R, T)$ for two values of R is shown in figure 5. The first thing that we notice is that the distribution is quite broad. This confirms the main assumption of generalized RFOT, reconciling the theory with the numerical data. If surface tension had a single value, a region smaller than ξ would not be able to rearrange, so a non-fluctuating surface tension implies a sharp drop of the point-to-set correlation $q_c(R)$ at $R \sim \xi$. With a fluctuating surface tension, on the other hand, *any* region can decorrelate, provided there are target excitations with surface tension $Y < T\Sigma R^{d-\theta}$. Our finding is thus consistent with the smooth decay of the correlation observed numerically [1, 2].
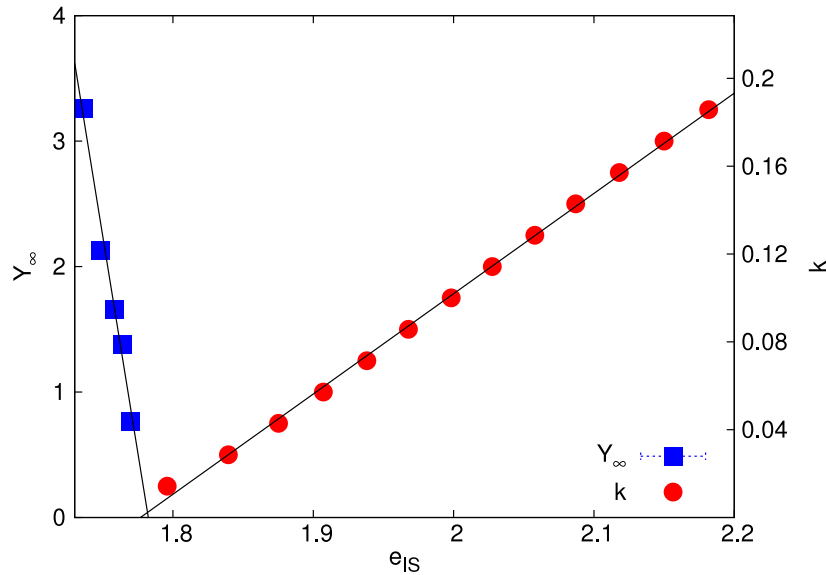
Figure 4. Left: Y_∞ (squares) versus parent IS energy. Right: intensive saddle instability index k (circles) versus IS energy (data from [12]). Lines are linear fits. Both the surface tension and the instability index seem to vanish at a similar energy, the threshold e_{th}, which is therefore the spinodal point.
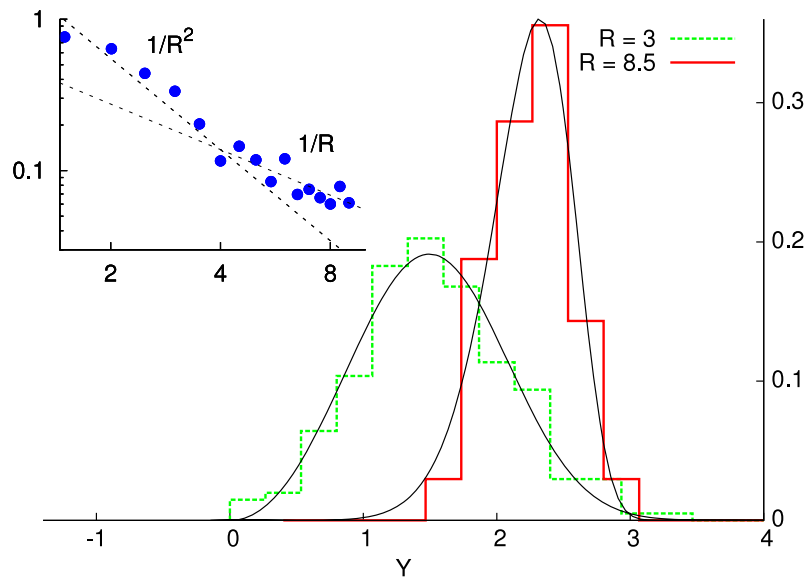

Figure 5. Normalized histograms of the surface tension for $T = 0.89\, T_c$ at two values of R. The values of Y are computed for all the hybrid ISs at a given R via the equation (3). Note that this distribution does not depend on the exponent ω and that its average tends to $Y_\infty(T)$ for $R \to \infty$. The distribution narrows on increasing R. Solid lines are fits to $P(Y) = -\mathrm{d}/\mathrm{d}Y \exp\left[-(Y/y_c)^\nu\right]$. Inset: variance of $Y_{\alpha\beta}$ versus R. At large R its decay is clearly slower than $1/R^2$. Note that $\mathrm{Var}[Y_{\alpha\beta}] = \mathrm{Var}[Y_\infty] + \mathrm{Var}[\delta_{\alpha\beta}]/R^{4-2\omega}$. For $\mathrm{Var}[\delta_{\alpha\beta}]$ independent of R and $\omega \sim 3/2$, $\mathrm{Var}[Y_{\alpha\beta}] \sim 1/R$, compatible with our data.

The second important result is that the distribution narrows as R grows. Since the relevant length scale is $\xi(T)$, we may assume that the physical properties depend only on

$$P(Y,T) \equiv P(Y, R = \xi(T), T). \tag{4}$$

This $P(Y,T)$ narrows as T decreases, because $\xi(T)$ grows. But $P(Y,T)$ is related to $q_c(R,T)$ by [2]

$$q_c(R,T) = \int_{T\Sigma R^{d-\theta}}^{\infty} P(Y,T)\, \mathrm{d}Y, \tag{5}$$

so when T decreases, the decay of $q_c(R,T)$ sharpens, in qualitative agreement with the numerical finding of [2].

The distribution is well fitted by $P(Y) = -\mathrm{d}/\mathrm{d}Y \exp\left[-(Y/y_c)^\nu\right]$ [2] (see figure 5). The complementary cumulative distribution $q_c(y) \equiv \int_y^\infty \mathrm{d}Y\, P(Y)$ is then $q_c(y) \sim \exp[-(y/y_c)^\nu]$. This is the same functional form as was used in [2] to fit the decay of the point-to-set correlation[10]. At the lowest temperature $T = 0.89\,T_c$ a fit of $q_c(y)$ yields $\nu \approx 4.2(1)$, encouragingly close to the value 4.0 ± 0.6 of [2]. This agreement between two completely different protocols puts the generalized RFOT on a firmer basis.

The present study provides evidence for the existence of amorphous excitations in glass-forming liquids, and of a surface tension distribution between such excitations with the properties required by a generalized RFOT. The average surface tension vanishes at e_{th}, meaning that a spinodal mechanism prevents these excitations from existing for configurations whose corresponding IS energy is higher than e_{th}. We stress once more that the spinodal transition is only visible if we choose energy, rather than temperature, as a control parameter. Therefore, using ISs rather than thermal configurations is not an arbitrary approximation, but rather a necessary condition for the surface tension analysis to be fruitful. The fact that the distribution of Y broadens for $e \to e_{th}$ implies that the transition will look smooth: instead of disappearing abruptly (as in the mean field [6]), metastable states slowly *fade out*, because excitations are becoming less and less costly on average and because states are slowly merging with each other.

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[10] Actually, the exponent describing the decay of $q_c(R)$ is $\zeta = \nu(d-\theta)$, but in our case the two are identical since $d = 3$ and $\theta = 2$.

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