Are defect models consistent with the entropy and specific heat of glass-formers?

Giulio Biroli
Service de Physique de Théorique, Orme des Merisiers,
CEA Saclay, 91191 Gif sur Yvette Cedex, France;

Jean-Philippe Bouchaud
Service de Physique de l'État Condensé, Orme des Merisiers,
CEA Saclay, 91191 Gif sur Yvette Cedex, France;
and Science & Finance, Capital Fund Management, 6-8 Bd Haussmann, 75009 Paris, France.

Gilles Tarjus
Laboratoire de Physique Théorique des Liquides, 4 Place Jussieu, 75231 Paris Cedex 05, France
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We show that point-like defect model of glasses cannot explain thermodynamic properties of glass-formers, as for example the excess specific heat close to the glass transition, contrary to the claim of J.P. Garrahan, D. Chandler [Proc. Natl. Acad. Sci. **100**, 9710 (2003)]. More general models and approaches in terms of extended defects are also discussed.

Kinetically constrained models (KCM) display trivial thermodynamics but non trivial dynamics [1–3]. They encapsulate in a specific way the 'free volume' idea according to which the slow dynamics of glasses is due to rare, localized mobility defects [4, 5]. For most KCMs, slow dynamics is indeed due to defect motions [3]. A remarkable aspect of these models is that although the dynamical rules are very simple and local, the emergent defect dynamics lead to highly non trivial physical behaviour. As a consequence KCMs provide a theoretical framework for understanding many of the remarkable dynamical properties of fragile glass-formers, such as super-Arrhenius relaxation time [3, 6, 7], dynamical heterogeneities [8–11] and viscosity/diffusion decoupling [12]. That these models may in fact describe *quantitatively* the physical properties of glasses has been strongly advocated in a series of papers by J.P. Garrahan and D. Chandler (GC) [9, 10], and investigated further in [13].

One of the major tenet of KCMs is the complete decoupling between dynamics and thermodynamics, at variance with the traditional view of Adam and Gibbs [14], and others [15, 16], in which the decrease of configurational entropy with temperature is the fundamental underlying mechanism for the viscous slowing down. It is therefore *a priori* surprising that KCMs could have anything sensible to say about the entropy and specific heat of real materials – even if these turn out to be acceptable models of their dynamics. Nevertheless, the claim made in [10] is that these models are also in quantitative agreement with the specific heat of these materials. More precisely, assuming a perfect gas of free defects, GC give a formula for the specific heat at fixed pressure per particle of the liquid (in excess of that of the solid), which we reproduce from ref.[10] to be:

$$\Delta C_p(T) = k_B \left(\frac{J}{T}\right)^2 c(T)\mathcal{N} + O(c(T)^2), \qquad (1)$$

where $\mathcal{N}$ is the number of physical molecules contributing to enthalpy fluctuations in a coarse-graining cell, J is the enthalpy cost, in kelvins, for creating a mobile cell (remember that liquids are considered here at constant pressure, hence the importance of distinguishing between enthalpy and energy). The concentration of mobile cells c is *assumed* to be given by $c(T)/(1 - c(T)) = A\exp(-J/T)$, where the numerical prefactor A is argued by GC to be rather large: $\ln A$ is akin to an entropy gain $\Delta s_0/k_B$ associated with the creation of a mobile cell. Note that there is a small difference between the specific heat in excess to that of the glass (considered in [10]) and that in excess of the crystal; this difference is however irrelevant for the present discussion.

In the following we first adress the results of [10] showing that even if the value of ΔC_p at T_g seems to match experimental values, the temperature dependence of ΔC_p predicted by Eq. (1) is in total disagreement with experimental values. We then discuss in detail the derivation of $\Delta C_p(T)$ and the physical assumptions behind Eq. (1). This derivation leads to a formula different from Eq. (1) and makes clear that the defect contribution to $\Delta C_p(T)$ is in fact completely irrelevant close to the glass transition. In order to avoid a contradiction, one has to assume that the main contribution to both the entropy and the specific heat comes from the *immobile* regions. Although this is most reasonable physically, it implies that the models considered by GC are incapable of reproducing the thermodynamics of fragile glasses (and actually neither of strong glasses).

A clean way to test Eq. (1), that gets rid of any ambiguity in prefactors (we in fact disagree with the prefactor $\mathcal{N}$ in Eq. (1), see below), is to rewrite it as:

$$\frac{\Delta C_p(T)}{\Delta C_p(T_g)} \approx t^{-2}\exp\left(\frac{J}{T_g}\frac{t-1}{t}\right) \qquad t = \frac{T}{T_g}. \quad (2)$$

This formula is expected to be valid for small $c \approx$

$A \exp(-J/T)$, where the description of glassy dynamics in terms of rare, dilute, defects could make sense – corresponding to a large enthalpy of creation for mobility defects, $J/T_g \gg 1$.

Using viscosity data *at fixed (atmospheric) pressure*, GC are able to estimate the value of J/T_g, found to be equal to 16.7 for 3-bromopentane (3BP) and 26.7 for ortho-terphenyl (OTP), indeed quite large compared to unity. Fig. 1, on the other hand, gives a plot of $\Delta C_p(T)/\Delta C_p(T_g)$, obtained from Eq. (2), as a function of T/T_g for $J/T_g = 10, 20, 30$ and compares it to the experimental values for 3BP [17] and OTP [18]. (Note the log scale on the y-axis.) It is clear that Eq. (2) is totally incompatible with the data when J/T_g is large: it varies much too fast with temperature, and increases with T instead of decreasing (a similar criticism has been made by C. Angell and coworkers [19] for excitation models).

An acceptable fit of the data with Eq. (2) requires $J/T_g \approx 1.3$, meaning that within this description the density of defects is not small at all – but this of course is then incompatible with viscosity data. For consistency, Eq. (1) cannot be used for temperatures such that $c \simeq 1$; GC restrict their analysis to a temperature range between T_g and $T_{1/2}$, where $T_{1/2}$ is defined as the temperature at which the logarithm of the viscosity expressed in Poise, or of the relaxation time expressed in picoseconds is half its value at T_g (see Fig. 1). One can clearly see that, even in this restricted interval of temperature close to T_g (for which c is of the order or less than 10^{-1} [10]), the theoretical prediction is in complete disagreement with the experimental data.

The previous discussion suggests that the thermodynamic predictions of the models considered in [10] are incompatible with experiments. As we discuss below, there is in fact no real contradiction: the order of magnitude of the defect contribution to the specific heat is simply much smaller than the experimental value between T_g and $T_{1/2}$, which is instead dominated by the thermodynamic properties of immobile regions. In the models considered in [9, 10], however, the immobile regions give a trivial contribution to thermodynamics properties. In order to be consistent, one should assume that these regions dominate the thermodynamics but are irrelevant dynamically.

Let us now reconsider in detail the derivation of Eq. (1) taking explicitly into account that experimentally *both* the specific heat and the excess entropy are found to be of order k_B per particle or larger at the glass temperature – indeed a very important "stylized fact" of fragile glasses. An immediate consequence of this experimental fact is that the excess entropy of the liquid cannot be due to point-like defects only: since these must be dilute to lead to large relaxation times, their contribution to the excess entropy must be small. Within a simple coarse-grained defect description, the total excess entropy per cell (with
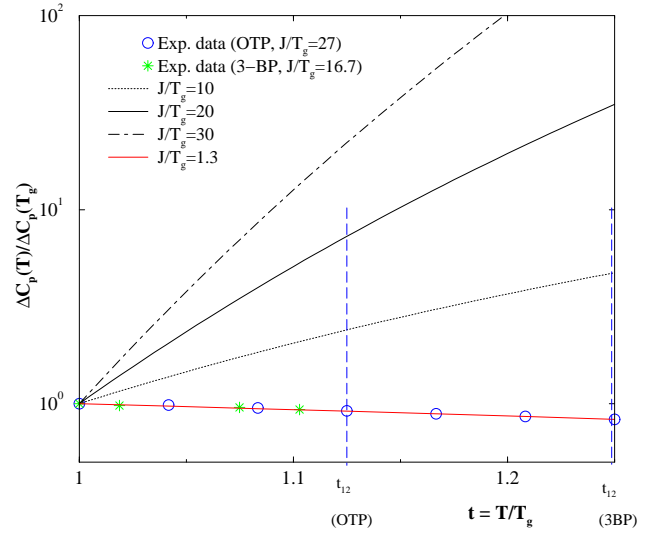

FIG. 1: Normalized excess specific heat as given by GC's formula, Eqs. (1) and (2), for $J/T_g = 10, 20, 30$, compared with the experimental data for OTP and 3-BP, for which GC estimate, from viscosity data, $J/T_g = 26.7$ and 16.7, respectively. Note the log scale on the y-axis. The two vertical lines correspond to $T_{1/2}$ defined as the temperature at which the logarithm of the viscosity expressed in Poise, or of the relaxation time expressed in picoseconds is half its value at T_g.

respect to the crystal), Δs, is:

$$\Delta s = -k_B[c \ln c + (1-c)\ln(1-c)] + c\Delta s_0 + \Delta s_c, \quad (3)$$

where the first term corresponds to the entropy of the ideal gas of defects, the second term to the entropy difference between mobile and immobile cells (see above), and the last term is the configurational entropy associated with frozen cells [21]. In order to get the experimental order of magnitude of Δs at T_g and at the same time have ΔC_p dominated by defect properties, one must assume that (i) Δs_c is of order $\mathcal{N}k_B$, hence much larger than the defect entropy itself; (ii) Δs_c must then be temperature independent, otherwise it would give the leading contribution to ΔC_p. Although large, the excess entropy Δs_c should not play any physical role in the slowing down of the material in this picture (in strong contrast with the view expressed in [14–16]). Therefore, the excess specific heat at constant pressure *per cell*, $\Delta c_p(T) = T d\Delta s(T)/dT$, is given by:

$$\Delta c_p(T) = k_B \frac{J}{T} T \frac{dc(T)}{dT} \approx k_B (J/T)^2 c(T), \quad (4)$$

where we have used $c(T) \approx \exp(\Delta s_0 - J/T)$, valid in the limit $c \ll 1$. Note that the functional form of $c(T)$ cannot be derived within the model and it is in principle obtained from the coarse-grained procedure that should map glass-forming liquids to KCMs. Since until now no such procedure has been developed one has to postulate

an a priori functional form $c(T)$. The simple physical assumptions described above correspond to the one assumed in [10]. However, we will show below that our conclusion is indeed independent of the form of $c(T)$. We have obtained a specific heat *per cell* given by $k_B(J/T)^2c$, and therefore a specific heat *per molecule* given by:

$$\Delta C_p(T) \approx k_B \left(\frac{J}{T}\right)^2 c(T)\mathcal{N}^{-1}, \qquad (5)$$

a factor $\mathcal{N}^2$ smaller than Eq. (1). The same expression is obtained by looking directly at the enthalpy fluctuations [22]. Taking very favorable values for the parameters $c = 0.01$, $J/T_g = 30$ and $\mathcal{N} = 10$ leads to $\Delta C_p(T_g) \approx 0.1k_B$, already a factor 100 too small compared to experimental values ($9k_B$ for 3-BP, $13k_B$ for OTP). The only way to avoid a contradiction is that the temperature dependence of Δs_c is strong, and that in fact all the thermodynamics is contained in that very contribution.

The above conclusion is based on comparing the experimental specific heat to that predicted by defects only. A more general argument (see also [16, 20]), independent of the shape of $c(T)$, relies on the entropy change between – say – T_g and $T_{1/2}$, which is experimentally found to found to be of order k_B ($\approx$ $4k_B$ for OTP). Thus, not only one finds that $\Delta s_c(T)$ has to be much larger than $(-k_B[c\ln c + (1-c)\ln(1-c)] + c\Delta s_0$ at T_g, as discussed previously, but also that $\Delta s_c(T)$ has to provide the leading contribution between T_g and $T_{1/2}$ since in this regime the ideal gas entropy of defects [23] is negligible [10]. As a consequence, using the relationship $\Delta c_p(T) = Td\Delta s(T)/dT$, one finds again that the main contribution to ΔC_p comes from the *immobile regions* close to T_g. Note that this result is independent of the functional form $c(T)$, as long as defects are dilute, $c \ll 1$, a necessary condition for the GC description to be useful [24].

So, are all KCMs (or more generally defect models) doomed to fail in describing thermodynamics? The point of view advocated in [9, 10] is that after having appropriately coarse-grained time and space a liquid can be strictly speaking considered as a KCM with trivial thermodynamics and simple kinetic constraints that induce slow dynamics. As we have shown, this line of thought is clearly insufficient to recover thermodynamics. Another point of view (see for example [2, 6]) is to only assume that the effective dynamics for a lattice model of a glass-forming liquids is characterized by some kinetic constraints. In this case the trivial thermodynamics is not necessary but just a choice of simplicity. A quantitative model (arising from a real mapping from liquid dynamics) would also contain effective interactions between particles and would therefore lead to non-trivial thermodynamics. One important fact remains though: even if the thermodynamics can be non trivial, it is only an indirect cause of slow dynamics, through the temper-

ature dependence of the defect density, and not a driving cause of the slowing down. In our view, any eligible theory of the glassy state has to produce a convincing explanation of the remarkable connection between thermodynamics and dynamics, more precisely between the configurational entropy and the relaxation time [26]. At the moment this seems to be an important missing piece in KCMs. Hopefully, future works on KCMs and their possible generalisations will unveil whether or not some of these models can pass this important test. A way to increase the entropy contribution of mobility defects and find a relationship between dynamics and thermodynamics seems to be through *extended defects*. This is the path followed (using different arguments) in [14–16, 27–29] (see also [30, 31] for quantitative computation of the excess configurational entropy in model systems). In all these scenarii, the presence of mobility regions, that are typically interfaces (e.g. domain walls), is driven by a thermodynamic mechanism with a (possibly avoided) critical point.

Addendum

In the following reply, Chandler and Garrahan have amended their original model which now allows for two different species of excited cells – most of them are in this new version immobile, and very few are mobile. Even though the microscopic justification of this ad hoc assumption is unclear, the new fitting parameter, the ratio of excited mobile to excited immobile cells, indeed allows one to obtain both a large specific heat jump and a large relaxation time. In such a framework, however, the strong connection between thermodynamical and dynamical fragility, which we emphasized above, becomes completely out of reach or very artificial (thermodynamics is dominated by immobile excited cells that are irrelevant as far as dynamics is concerned). We also note that despite the introduction of another fitting parameter [the temperature dependence of the ratio of excited mobile to excited immobile cells] the theory proposed by Chandler and Garrahan still leads to a specific heat which has the wrong temperature dependence – note that the scale of the y-axis in their Fig. 1 makes it hard to see that their prediction for the excess of specific heat is in fact increasing with temperature, in contradiction with experiments that clearly show an opposite trend. It might be possible, by introducing additional assumptions and fitting parameters, to obtain yet another version of Chandler and Garrahan's model that "accounts for" these basic experimental facts. However, all this is at the expense of the simplicity, the predictive power and, more importantly, the very meaning of the underlying physical picture.

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[23] Even if there was a static interaction between defects, the entropy contribution cannot be larger than the ideal gas one.

[24] This in principle does not directly apply to strongly cooperative defect models. Their structural relaxation timescale (and inverse of the defect density) can increase extremely fast when the temperature decreases or the particle density increases [2, 3, 6]. But at the same time their entropy decreases mildly and smoothly in such a way that it is not necessary to have a very small entropy in order to have a very large relaxation time [25].

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