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LETTER TO THE EDITOR

Glasses under high pressure: a link to colloidal science?**Th Voigtmann and Wilson C K Poon**SUPA and School of Physics, The University of Edinburgh, Mayfield Road,
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Online at stacks.iop.org/JPhysCM/18/L465**Abstract**

Whether glass formation is mainly driven by temperature or by pressure is an open question that is now being addressed in high-pressure experiments. Here we propose that some insight into these questions could be gained by comparing in a suitable manner with colloidal glass-transition data. Based on such a comparison, a cross-over is found from the usual regime of molecular glasses (where temperature effects tend to be important) to a very-high-pressure regime (where density effects eventually take over). This regime is found to be located at pressures higher than commonly studied in today's glass-transition experiments.

Molecular and polymeric glasses have been studied intensely for well over a century, and yet significant puzzles remain. There is considerable debate about what the driving force is behind the glass transition. It could be mainly a free-volume (or density, or pressure) phenomenon, since glass formers are typically dense liquids where core-repulsion effects are large. It could however also be a dominantly energetic (temperature-driven) phenomenon, as it clearly is in bonding-driven network-forming glasses such as silica. In recent years, a large number of experiments under elevated pressure have been carried out to address this debate (many of them reviewed in [1]). The results are far from unequivocal: it is not clear whether at high pressure the dynamics becomes more and more free-volume driven or not, and if this is universal behaviour or not.

The controversy has also led to a split of glass-transition research into two largely disjoint communities: molecular and (small-)polymeric glass formers on one side, colloidal suspensions on the other. The idea of viewing colloids as big atoms goes back to Einstein and Perrin, and for *equilibrium* phenomena this analogy now is a valuable routine [2]. But for *non-equilibrium dynamic* phenomena, it is unclear how far such an analogy, if it exists at all, can go. The glass transition is a prime example: it is a dynamic arrest that is observed in both molecular glass formers (changing temperature T or pressure P) and colloidal suspensions (usually upon changing their number density ρ). But many such model colloids are good representatives of hard-sphere systems which show no energetic effects. If the latter are important for molecular

glasses, the hard-sphere-like colloidal glasses must be, despite all similarities, of a different kind, as has been argued before [3].

The inclusion of energetic interaction effects in colloidal glasses has been studied quite recently, through the use of model colloid–polymer (CP) mixtures: hard-sphere suspensions in which added free polymers induce a ‘depletion’ attraction between the colloidal particles [2], of both tunable range δ (relative to the hard-sphere diameter d) and effective strength ($U_0/k_B T$, a function of polymer concentration c_p). This degree of control makes CP mixtures fascinating systems for investigating the role of different interaction types at the glass transition. Such understanding is also highly relevant and sought after for molecular glasses.

Here, we investigate in which sense our understanding of ‘real-world’ molecular glasses can benefit from the CP-mixture studies. We focus on a single characteristic feature here, namely the glass-transition line in the pressure–temperature plane, $P_g(T)$ or $T_g(P)$. There is of course more to the glass-transition dynamics than this, but one may assume that the way $P_g(T)$ depends on T encodes information about how temperature and free-volume effects enter glassy dynamics. We are not concerned with the actual numbers of P_g or T_g , but only with their qualitative trends. In brief, we compare the trend observed in recent colloidal data [4, 5] with that observed in molecular glass formers and conjecture that, if they are equal, there is likely to be a deep similarity concerning the physical mechanisms at work in both system classes.

Such a mapping has not been tried previously (to our knowledge), because colloidal physics tends to deal with hard-sphere density ρ and interaction strength U_0 as the natural control parameters. One needs a reliable equation of state (EOS), $P/k_B T = Z(\rho, T)$ to construct from the available $\rho_g(c_p)$ data the CP-mixture $P_g(T)$ line¹. This is usually not known for the complex fluids of interest here. Furthermore, it turns out that the expression for the EOS needs to yield qualitatively correct results over a huge range of (ρ, T) values—not the case for many ad hoc approximations. Fortunately, the glassy dynamics of CP mixtures is well described by a relatively simple model potential, the square-well (SW) model: a hard core, $U(r) = \infty$ for $r < d$, supplemented with an SW attraction of range δ , $U(r) = -U_0$ for $d < r < d(1 + \delta)$, and $U(r) = 0$ elsewhere. For the SW model, an EOS approximation can be obtained, building on the work of [6], where the static structure factor was derived (within the mean-spherical approximation and for δ not too large). We thus obtain an analytical expression for $Z(\rho, T)$. Using this, we have been able to transform the CP-mixture glass-transition line into the P – T plane. Note that this mapping does not depend on a theory of the glass transition, although we shall later compare with mode-coupling theory (MCT) results. Now, we only require a choice of parameters for calculating the SW EOS. We take $\delta = 0.044$ and $U_0/k_B T = c_p \cdot 2.3 \text{ cm}^3 \text{ mg}^{-1}$, employing natural units for an SW system, T in units of U_0/k_B , and P in units of U_0/d^3 . We also scale φ by 0.89 to ease the later comparison with MCT (this maps the experimental hard-sphere transition point onto the theoretical one).

The result of the transformation is shown in figure 1. A double-logarithmic representation is adequate, since the data (shown as stars) span several orders of magnitude in both variables. The hard-sphere experiment in fact corresponds to the point $T = \infty$ in this representation. In the $(\log P, \log T)$ representation, the glass-transition line for the CP mixture consists of three regimes. (A) $P \gtrsim 1$, where the glass-transition pressure is linear in T , i.e. it follows a hard-sphere isochore. This is the density-driven hard-sphere-like glass transition expected for $U_0 \rightarrow 0$. (B) $0.1 \lesssim P \lesssim 1$, where $\log P_g(\log T)$ exhibits an almost vertical steep increase with $\log T$. One can call this a ‘temperature-driven’ section (since verticals represent isotherms), although this is subtly different from an ‘energy-driven’ transition; see below. (C) $P \lesssim 0.1$, reflecting a dilute system of sticky hard spheres.

¹ For colloidal systems, we identify with P the *osmotic* pressure of the dispersion.

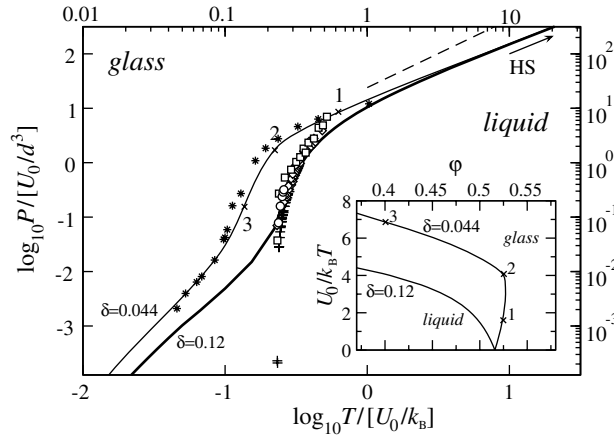


Figure 1. The glass transition in the pressure–temperature plane, in natural units for hard spheres (diameter d) with square-well attraction (range $\delta \times d$, depth U_0): experimental data from colloid–polymer mixtures (*) [4, 5] (the hard-sphere data point is indicated by an arrow to $T \rightarrow \infty$); experimental data for small-molecular and polymeric glass formers *o*-terphenyl (+ symbols, $P_0 = 0.76$ GPa, $U_0/k_B = 1057$ K) [7–9], glycerol (\diamond , $P_0 = 3.09$ GPa, $U_0/k_B = 826$ K) [10, 12], dibutylphthalate (\square , $P_0 = 0.79$ GPa, $U_0/k_B = 765$ K) [12], and poly[(phenyl-glycidyl-ether)-co-formaldehyde] (\circ , $P_0 = 0.75$ GPa, $U_0/k_B = 1148$ K) [11]. Lines are mode-coupling theory predictions for the square-well system with $\delta = 0.044$ and $\delta = 0.12$. The dashed line indicates the soft-sphere asymptote, $P \propto T^{5/4}$. Inset: MCT lines in the usual density–attraction-strength representation. Points 1–3 correspond in the two plots.

Let us now recapitulate how the molecular glass transition appears in the $\log P$ – $\log T$ plane. To this end, we have collected some representative data sets from the literature [7–12]; a focus was put on experiments that have probed very high pressures. A rescaling of units is needed in order to relate the standard units [P] = Pa and [T] = K to the canonical SW units. Again, we are not concerned with absolute numbers: for example, the glass transition temperature T_g (the point where the viscosity of the glass-forming liquid reaches 10^{12} Pa s) at ambient pressure varies due to the different chemical structures of the different liquids. We therefore rescale the data such that this change is absorbed into the scaling; this essentially implies that we scale temperature with some (effective) intermolecular-interaction strength. Similarly, from the different numerical values of the density at ambient conditions (i.e., the different size and shape of different molecules), we expect an intrinsically different pressure range; we again absorb this into a rescaling. Note also that our approximate EOS is likely to introduce a shift in the T -scale [6], also absorbed into the scaling. To relate temperature scales, we set $U_0 = 0.23k_B T_g$ for all the molecular data shown. A scaling factor P_0 for the pressure axis then is obtained by requiring $\rho(U_0/P_0) \approx \text{const}$. Here, T_g and ρ are the experimental glass-transition temperature and number density of the liquid at ambient conditions. In our mapping, we use $P_0 = (\rho U_0)/(0.04 \pm 0.015)$, which as a rule of thumb identifies $P/[U_0/d^3] = 1$ with ≈ 1 GPa for typical (‘fragile’) glass formers. Note that the procedure allows us to shift around the molecular glass-transition curves in the $\log P$ – $\log T$ plot, but *without distortion*. The feature we want to focus on is the *shape* of the $\log P_g(\log T)$ curve, and to a lesser extent its position along the P -axis.

The molecular data are shown in figure 1 as open symbols and crosses. These data all group around each other, and around $T \approx 0.3$. The data collapse is not perfect, nor is it supposed to be: the pressure coefficient of the glass transition, dT_g/dP , is not a material-independent

quantity, and scaling relations involving T^γ with some material-dependent exponent γ have been found to work [1]. But on the scale of our figure, these differences do not matter. In particular, the data show a bend from a steep region around $T \approx 0.3$ (regime B) to a flatter region (A) that is reminiscent of half the S-shape observed for the colloidal glass-transition line. However, most of the current molecular data remain in regime (B), where the transition appears to be ‘temperature driven’. Let us stress that, while temperature will eventually be the most effective control variable, it does not imply a statement about density effects becoming negligible. To understand why there is a generic drop in the GT lines in regime (B), a theory is needed. We will give such an account elsewhere; here, we want to proceed with as little theoretical bias as possible.

Figure 1 leads us to propose a generic cross-over from a ‘temperature-driven’ to a ‘density-driven’ glass transition as the pressure is increased. This is reasonable, since ultimately, at extremely high pressure, all dynamics will essentially probe the core-repulsion part of the interparticle interactions. As long as a description in terms of molecular pair potentials such as the Lennard-Jones (LJ) system continues to be applicable, the $P \rightarrow \infty$ asymptote of the glass transition line in molecular liquids will then be an isochore of the form $P_g(T)/T \sim T^{1/4}$, indicated by a dashed line in the figure. The data in figure 1 support this. One can absorb the soft-core effect into a temperature-dependent effective diameter. Doing so, the asymptote will be the same as the one shown for the colloidal hard-sphere-like data, while the shape of the curve in regime (B) is essentially unchanged. To test this claim for molecular liquids, the figure also suggests a pressure scale: regime (B) will only be entered for pressures exceeding the 10 GPa mark. To date, only the experiments of [12] are close enough to have indicated such a cross-over.

A remark is in order about the low- T regime (C): this is only visible in the colloidal data. Here, colloidal gelation occurs, something not observed in molecular liquids. Furthermore, from the analysis of the colloidal dynamics [6, 4], one knows that this is a truly attraction-driven transition, where density effects can ultimately be neglected. Our comparison indicates that this regime is never entered for molecular data.

Let us finally comment on the different positions of the data sets along the $\log T$ -axis: even taking into account some uncertainties in our rescaling of units, the difference between the CP-mixture and the molecular-glass data is significant. Crucially, the steep part of the data groups, regime (B), is located at around $T \approx 0.1$ for the colloidal data, about a factor of three lower than the molecular data. There is an obvious factor explaining this: the typical interaction range differs—from around 10–20% of the core diameter in molecular liquids to around only 4% in the SW model. One could in principle obtain experimental data also for CP mixtures with a larger interaction range; unfortunately, we found no such data available. Still, we can understand the effect of a change in interaction range on the $\log P_g(\log T)$ curve. For this we apply MCT to the SW model [6] and calculate the glass transition line for different δ (solid lines in figure 1). According to this calculation, a change from the CP-typical $\delta = 0.044$ to $\delta = 0.12$ (inspired by the minimum position of the LJ potential) brings about exactly the shift along the $\log T$ -axis discussed above, suggesting that (details of our scaling procedure notwithstanding) the difference in the typical position of regime (B) is indeed an interaction-range effect. In molecular glasses, the MCT transition point T_c differs from the shown T_g , but this difference is of no concern here: T_c roughly marks an iso-viscosity line, and, e.g., $T_c(P)$ measured for *o*-terphenyl lies slightly to the right of the data in our figure, showing the same trend as $T_g(P)$ [13], which is an iso-viscosity line by definition. For the reader more versed in the conventional representation, the inset of figure 1 also shows the same results in the (ρ, U_0) plane. As this inset demonstrates, the smaller interaction range also results in a wealth of new phenomena (among them reentrant isochores) [4, 6], with which we are not concerned here.

To conclude, we have suggested that conventional molecular glasses and colloidal glasses have in common the physical interpretation of the way their glass transition changes with pressure and temperature. This opens a connection between the two kinds of systems that has recently received little attention: it suggests that one can use colloidal systems, taking advantage of the fine control they offer over the interaction potential, in order to gain insight into some open questions being asked in the field of molecular glasses. As a first example, we estimate the pressure one needs to exceed in order to reveal a properly density- or pressure-driven glass transition in molecular glass formers. Our estimate is 10 GPa, higher than the pressures reached in previous dynamic experiments at high viscosities, explaining why the controversy is still alive. Extremely-high-pressure experiments on molecular glass-forming liquids, accessing this regime, would in our opinion be of great value.

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