Idealized glass transitions under pressure: dynamics versus thermodynamics

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The interplay of slow dynamics and thermodynamic features of dense liquids is studied by examining how the glass transition changes depending on the presence or absence of Lennard-Jones-like attractions. Quite different thermodynamic behavior leaves the dynamics unchanged, with important consequences for high-pressure experiments on glassy liquids. Numerical results are obtained within mode-coupling theory (MCT), but the qualitative features are argued to hold more generally. A simple square-well model can be used to explain generic features found in experiment.

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The quest for identifying the physical mechanism behind the dynamical transformation of a liquid into an amorphous solid, the glass transition, has prompted many studies aiming to disentangle the dominant control variables involved. It is recognized that the slow dynamics connected with the glass transition is universal, but its connection to the underlying liquid structure is highly debated [1, 2, 3, 4, 5]. Some argue in terms of entanglement, but its connection to the underlying liquid structure is uniaxial. Many studies aiming to disentangle the dominant contributions to the dynamical transformation of a liquid into an amorphous solid have been carried out [23, 24, 25, 26, 27], some with density dependence [15, 16, 17, 18, 19, 20, 21, 22], some with temperature dependence [6, 7, 8, 9]; some that it does not [10, 11, 12]. Others find that temperature dominates glassy dynamics by far [28, 29, 30, 31]. The difficulty of obtaining data over a wide pressure range makes this an impediment: few studies, pioneered only in the 1990’s [28, 32], go beyond 1 GPa.

Here we propose that to resolve the apparent contradictions, one needs to separate non-universal thermodynamic aspects, namely the equation of state (EOS) of the idealized glass transition with that of its purely repulsive (LJ) counterpart. The interplay of slow dynamics and thermodynamic features of dense liquids is studied by examining how the glass transition changes depending on the presence or absence of Lennard-Jones-like attractions. Quite different thermodynamic behavior leaves the dynamics unchanged, with important consequences for high-pressure experiments on glassy liquids. Numerical results are obtained within mode-coupling theory (MCT), but the qualitative features are argued to hold more generally. A simple square-well model can be used to explain generic features found in experiment.

The Lennard-Jones (LJ) potential serves as a realistic interaction model: $V_{LJ}(r) = 4\epsilon[(r/\sigma)^{12} - (r/\sigma)^{6}]$, with dimensionless parameters $\phi^* = \rho\sigma^3$, $T^* = 1/(\beta\epsilon)$, $P^* = P\sigma^3/\epsilon$; $\beta = 1/(k_B T)$ with Boltzmann’s constant $k_B$. To study relative effects of entropy and energy, we compare the LJ glass transition with that of its purely repulsive (LJR) counterpart, $V_{LJR}(r) = V_{LJ}(r) + \epsilon \geq 0$ for $r \leq 2^{1/6}\sigma$, $V_{LJR}(r) = 0$ else. For the transition lines, mode-coupling theory (MCT) [33, 34] provides a reasonable qualitative description. Its transition temperature $T_c$ is systematically above the experimental (calorimetric) one, $T_g$, but nevertheless serves as a good indicator for the change from high-$T$ liquid-like dynamics to low-$T$ glassy-like one [35, 36]. In MCT, $T_c$ is the point where the glass form factor $f(q)$, measuring an elastic response to the scattering spectrum, jumps discontinuously (usually from zero to a finite value) due to a bifurcation in $V(q)$.

$$f(q) = \frac{\rho S(q)}{2q^4} \int \frac{d^Dk}{(2\pi)^D} V(q,k) f(k)f(p),$$ (1)

$$V(q,k) = S(k)S(p)(q^2 - qk/S(k) - qp/S(p))^2/\sigma^2,$$ with wave number $q = |q|$, $p = |q - k|$. Equation (1) is solved numerically by an iteration scheme [37]. The interaction potential $V(r)$ and temperature $T$ enter only through the static structure factor $S(q)$, obtained in the hypernetted-chain (HNC) approximation [38, 39]. $S(q = 0)$ determines the pressure through the EOS,

$$\beta P = \int_0^\infty d\sigma \, S(q = 0, \sigma, T)^{-1},$$ (2)

integrated numerically for the LJ and LJR systems. We have checked that the quantitative error of the HNC closure does not influence our results qualitatively.

The MCT glass transitions for the two systems are almost identical, i.e., they depend very little on the presence or absence of attractive interactions. As shown in Fig. 1, the lines in a $T$-$\phi$ diagram coincide on the scale of the figure. In fact, most of the change in $T_c(\phi)$ can be understood from the soft-sphere limit: for $q \sigma^3 \geq 1$, $V_{LJ(R)}(r) \sim \epsilon(r/\sigma)^{-n}$, $n = 12$, and the only control parameter is an effective packing fraction, $\varphi_{eff} = (\pi/6)\sigma_{eff}^3$, where $\sigma_{eff}^3 = \sigma^3 T_c^{-3/n}$ accounts for the soft core. The dash-dotted line in Fig. 1 corresponds to this soft-sphere glass transition, $\varphi_c \approx T_c^{-3/n}$, where Eq. (1) yields $\varphi_{eff} \approx 0.564$. It clearly shows the same qualitative behavior as the $T_c(\phi)$ lines for the full LJ system. Molecular-dynamics simulation data on the LJ glass transition collected in Ref. [40] and estimates from energy-landscape calculations of Ref. [41] are reproduced in Fig. 1 as triangles. They agree with our results reasonably well, considering the different definitions of the glass-transition point used in these works.
Attractors have a crucial effect on the thermodynamics: they introduce a gas-liquid spinodal, whose estimate is shown in Fig. 1 (dotted line). The compressibility diverges smoothly there, $1/S(q = 0) → 0$. Hence, the resulting $P(\rho, T)$ values in the liquid, Eq. (2), are significantly lower with than without attractions, i.e., for $T < T_{\text{cr}}$ and $\rho > \rho_{\text{cr}}$, where $(\rho_{\text{cr}}, T_{\text{cr}})$ is the gas-liquid critical point. This even holds for approximations that fail to predict the spinodal (such as HNC), but replace it with branch points where $S(q = 0)$ is large [42]. In other words, LJ-like attractions in high-density liquids simply affect the pressure: the contributions of all particles add up to a flat background that does not influence the forces [43], nor the (glassy) dynamics.

Figure 2 demonstrates the marked effect the spinodal has on the glass transition line in the $P$-$T$ diagram: although nearly indistinguishable in the $T$-$\rho$ diagram, Fig. 1, the transition lines with (LJ) and without (LJR) attraction (solid thick and dashed lines) now appear qualitatively different. The LJ log $P_\varepsilon$-versus-log $T$ line has a steep part not present in the LJR line at $\log_{10} T^* < 0.1$, corresponding to $T^* < T^*_{\text{cr}} ≈ 1.4$. It stops at the spinodal, restricting the glassy regime to densities $\rho > \rho_{\text{cr}}$ [46]. Simulation data from Refs. [40, 44] (triangles in Fig. 2) scatter between the LJ and LJR lines since the simulations used different truncations of the potential, yielding different equations of state. The data from Ref. [40], where full $(\rho, T, P)$ triplets are given for several truncations, collapse to a single curve in Fig. 4 within error bars, confirming our finding.

The above results are easily understood within MCT: the glass transition in dense systems is driven by nearest-neighbor interactions (the cage effect), i.e., by features of the structure factor $S(q)$ at $q ≈ 2\pi/\sigma$. But the presence of attractions affects only $S(q → 0)$ [47]; a region strongly suppressed in the MCT integral, Eq. (11). Merely the transformation $\rho → P$ is dominated by $q → 0$ effects.

Since this transformation in general relies on straightforward but cumbersome numerical calculations, we simplify matters by introducing a square-well (SW) potential as a ‘cartoon’ of the LJ model, showing first that the qualitative features discussed above are still preserved. The SW model consists of a hard-sphere core and an attraction of relative width $\delta$: $V_{\text{SW}}(r) = -\epsilon$ for $1 < r/\sigma < 1+\delta$. Here, a mean-spherical approximation (MSA) for $S(q)$ [48] allows to integrate Eq. (2) analytically, greatly simplifying calculations. The MCT line for $\delta = 0.12$ [47] is shown in Fig. 2 rescaled as $T^* → 1.5 T^*$ to account for the different $S(q)$ approximation that mainly induces a shift in the $T^*$ scale [48].

We identify two generic regimes for both the LJ and the square-well lines: $T^* → \infty$ is the hard-sphere limit where the glass transition occurs along an isochore $P_\varepsilon \sim k_B T$; this limit is approached for $T^* > 1$ (regime I). It is also present in the LJ system, provided one corrects for soft-core effects, $P_{\varepsilon,\text{eff}} = P^* T^{3/4}$, as the dash-dotted line shows. For $0.1 \lesssim T^* \lesssim 1$ the steep log $P_\varepsilon$-versus-log $T^*$ line discussed above is found in both models (regime II). Its position along the $T^*$ axis scales with the gas-liquid critical temperature ($T^*_{\text{cr}} ∼ \delta$ for the MSA-SW). For $T^* → 0$, the SW model shows a low-density regime corresponding to densities $\rho < \rho_{\text{cr}}$ (a cross marks the point where $\rho_{\text{c}} = \rho_{\text{cr}}$), where the dynamics itself strongly depends on the potential depth $\epsilon$. This attraction-driven regime may be connected with colloidal gelation and
is absent in the Lennard-Jones model and in common molecular glasses. Relevant for typical glass formers at MPa pressures is regime II, as pointed out in a recent study \[41\]: experiments reveal steep $P(T_g)$ curves that are incompatible with the hard-sphere-like regime I. Diamond symbols in Fig. 2 exemplify this for glycerol: experimental $T_g(P)$ data from Refs. \[22, 23, 24, 25, 26, 27, 28, 29\] was mapped according to $\epsilon/k_B = 500$ K and $\epsilon/\sigma^3 = 2.5$ GPa, just to demonstrate qualitative agreement (and absorbing the quantitative difference between $T_g$ and $T_c$ in the mapping).

Our discussion of glass-transition lines has direct implications for dynamical quantities, as the latter are expected to depend strongly on the distance to the transition. For example, a ‘thermodynamic scaling’ has been observed for many glass formers, that involves

$$E/\nu^\gamma = (\partial \log \tau/\partial T^*)^{-1} \nu/(\partial \log \tau/\partial T^*) \nu, \quad \text{trivially related to} \quad E = (\partial q/\partial T)_{\tau}(\partial T/\partial \nu),$$

where $|E|$ signify a temperature-driven transition, small $|E|$ a density-driven one. $E$ consists of a glass-transition part, and a purely EOS-driven one. According to Fig. 1, the isokinetic term $r = (\partial q/\partial T)_{\tau}$ does not depend on LJ-like attraction; the EOS term $t = (\partial T/\partial \nu)_{\tau}$ however changes. Estimating the latter through the SW-MSA expression, we find that in fact, $t$ decreases in the vicinity of the spinodal: the measure $|E|$ increases with $P$, indicating a growing influence of temperature at higher pressures. Such trends have been found in experiments and argued to be at odds with the expectation that the transition becomes hard-sphere like at high $P$. According to our model, they are dominantly thermodynamic effects.

A similar conclusion holds for the pressure dependence of ‘fragility’ often used to classify how quickly relaxation times diverge. Recent work debated its relation to $q \rightarrow 0$ quantities such as elastic constants, the above energy-enthalpy ratio or the effective exponent $\gamma$. $\gamma$ is an empirical, effective exponent: even in the LJ system, $\gamma \neq 1/4 = 3/n \frac{4}{5}$. Is in agreement this, we find that the LJ transition line can be well fitted for all $T^* < 3$ by $g^*(T) \propto T^\gamma$, where $\gamma = 0.15 \ldots 0.23$. Partly, this merely mirrors that effective power laws can be used to fit the potential in the respective $V(r)/\epsilon \approx T^*$ range. If attractions are present, the effective $\gamma$ also depends on their details, as strikingly demonstrated by the SW system, where we do not find the $\gamma \rightarrow 0$ expected from the $n \rightarrow \infty$ hard-sphere limit.

One can characterize the relative effects of temperature and pressure on the glass transition by monitoring the viscosity $\eta$ along isotherms and isobars, using density as a parameter. Experiments \[5, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29\] usually find stronger variations along an isobar (varying $T$) than along an isotherm (varying $P$). This is a natural consequence of our scenario, evidenced in Fig. 3 by the viscosity $\eta^*$ in SW units, calculated from the standard Green-Kubo expression in MCT approximation \[33\]. Consider regime II: changing $T$ along the $P^* = 0.316$ isobar (solid line) corresponds to a more direct approach to the glass transition line as compared to changing $P$ along the $T^* = 0.3$ isotherm (dashed); cf. the thick arrows in Fig. 2. Clearly, $\eta^*$ diverges over a smaller density interval along the isobar. The agreement with experiment is semi-quantitative, as the symbols, reproduced from Ref. 17, demonstrate. Only in regime I (inset of Fig. 3) thin arrows in Fig. 2 do $P$ and $T$ exert equal influence. Not all transition points are equal: MCT predicts nonuniversal amplitudes and shapes for relaxation spectra that change along the transition line, invalidating a ‘temperature–pressure’ superposition principle. But the changes are small enough to make it appear to work, explaining why some experiments find it \[12, 13, 14, 15, 24, 45\], some with restrictions \[22, 54, 53, 56\], some not at all \[23, 57\].

Temperature- and density-effects are often quantified by a ratio of activation energy and enthalpy \[6, 31, 58\], $E_V/H_P = (\partial \log \tau/\partial T^{-1})_{\nu}/(\partial \log \tau/\partial T^{-1})_P$, trivially related to $E = (\partial q/\partial T)_{\nu}(\partial T/\partial \nu)_{\nu}$. Large $|E|$ signify a temperature-driven transition, small $|E|$ a density-driven one. $E$ consists of a glass-transition part, and a purely EOS-driven one. According to Fig. 1, the isokinetic term $r = (\partial q/\partial T)_{\nu}$ does not depend on LJ-like attraction; the EOS term $t = (\partial T/\partial \nu)_{\nu}$ however changes. Estimating the latter through the SW-MSA expression, we find that in fact, $t$ decreases in the vicinity of the spinodal: the measure $|E|$ increases with $P$, indicating a growing influence of temperature at higher pressures. Such trends have been found in experiments and argued to be at odds with the expectation that the transition becomes hard-sphere like at high $P$. According to our model, they are dominantly thermodynamic effects.

In conclusion, MCT glass-transition lines for the Lennard-Jones system and for the same system truncated to be purely repulsive are nearly identical in a $P-T$ plot, Fig. 4. Yet, they appear quite different in a $P-T$ diagram, Fig. 2. The difference can be understood as unrelated to the glass-transition mechanism itself, but to a difference in thermodynamic behavior only. If one accepts that the
glass transition is a primarily dynamic phenomenon, it will not be altered by sufficiently long-ranged, LJ-like, attractions. However, the equation of state, determining the pressure of the system, will change. The $P_c$-versus-$T$ curve hence has two regimes if attractions are present. In the very-high pressure regime I, it is essentially a density-driven fluid-glass transition: $P_c \propto T$, after correcting for soft-core effects. In regime II, identified as the experimentally relevant one, the existence of a gas-liquid spinodal leads to $T_c(P)$ curves with a much weaker $P$-dependence: this could be called a “temperature-driven” liquid-glass transition; but “temperature driven” is not equivalent to “attraction dominated”. Key qualitative features can be understood with the help of the square-well system as a better tractable model.

Discussing the glass transition in terms of “temperature vs. pressure” might obscure the physics responsible for it, focusing too much on different thermodynamics of different glass formers. For example, a change in composition in metallic glass formers greatly changes the thermodynamics, but has little effect on the slow dynamics [61]. Experiments probing the pressure range $P \gtrsim 1$ GPa seem desirable to test the picture proposed here.

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