

## The fragility of liquids and colloids and its relation to the softness of the potential

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# The fragility of liquids and colloids and its relation to the softness of the potential

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A parameter that is often used to characterize the dynamics of supercooled liquids is the dynamic fragility, however it is still debated how the fragility is related to other physical properties. Recent experimental data on colloidal systems have found that fragility decreases with increasing softness of the intermolecular potential. This result is in apparent disagreement with recent molecular dynamics simulations reporting the opposite behavior. Herein, using the thermodynamical scaling exponent  $\gamma$  as a measure of the steepness of the potential we show how these different results can be reconciled and also agree with previous results obtained for the dynamics of supercooled liquids at high pressures. [<http://dx.doi.org/10.1063/1.4768267>]

## I. INTRODUCTION

A supercooled liquid is a liquid cooled down rapidly below its melting temperature to avoid any crystallization.<sup>1</sup> A remarkable feature of the supercooled liquids is the continuous increase of their viscosity by more than ten orders of magnitude over a limited range of temperature. Eventually, the viscosity is so high that the supercooled liquids become metastable solids, i.e., glasses. This phenomenon is called the glass transition and remains one of the unsolved problems in condensed matter physics. Probably, the most puzzling aspect of the glass transition is that the spectacular increase of viscosity and the slowing down of the associated molecular motions that bring the formation of a glass occur without any apparent structural change.

Because of this feature, a measure often used to differentiate supercooled liquids is the rapidity with which their viscosity increases with decreasing temperature; this can be quantified by defining the steepness index or fragility,  $m_{p_0}$ :<sup>2</sup>

$$m_{p_0} = \left. \frac{\partial \log(x)}{\partial (T_g/T)} \right|_{T=T_g}, \quad (1)$$

where  $x$  represents the viscosity ( $\eta$ ), the structural relaxation time ( $\tau$ ), or other dynamical quantity.  $T_g$  is the glass temperature which is operatively defined as the temperature for which  $\tau(T_g) = 100$  s and  $\eta(T_g) = 10^{12}$  Pa s. These different operational definitions have been found to give close values of  $T_g$ .

In Eq. (1) the subscript “ $p_0$ ” indicates that the definition of fragility usually refers to the steepness index calculated in isobaric condition at atmospheric pressure. The isobaric steepness index,  $m_p$ , varies with pressure, increasing with increasing pressure for hydrogen bonded liquids and decreasing with increasing pressure for “simple liquids.”<sup>3</sup>

The progressive slowing down of the dynamics on approaching the glass transition is generally interpreted either as due to a reduction of the thermal energy causing a progressive confinement in the energy landscape or due to a reduction of the liquid density causing a progressive crowding of the molecular motions. However, during isobaric measure-

ments it is practically impossible to distinguish the two possible effects, since both temperature and density vary. A recent important result on disentangling the effect of  $T$  and density was obtained by high pressure measurements, from which it was established the validity of the so called thermodynamical scaling<sup>4,5</sup>

$$x(T, V) = f(TV^\gamma), \quad (2)$$

where  $f$  is a generic function,  $V$  is the specific volume, and  $\gamma$  is a material constant with typical values between 1 and 8.5.<sup>6</sup> This behavior has been now verified by many groups for a very large number of materials and also in molecular dynamics (MD) simulations.<sup>7–17</sup>

The origin of the thermodynamical scaling is not purely empirical; in fact, it was predicted for the case of liquids in which the molecular potential in the vicinity of its minimum can be described by the inverse power law,<sup>18</sup> and for this case the exponent  $\gamma$  is predicted to be one third of the exponent of the inverse power law. The validity of this interpretation has been confirmed by MD simulation in which varying the potential allows different values of  $\gamma$  to be obtained and these correlate well with the values of the exponent describing the repulsive potential.<sup>19,20</sup> Therefore, the parameter  $\gamma$  determined from the thermodynamical scaling can be considered an experimental measure of the steepness of the repulsive potential of supercooled liquids.

From the thermodynamical scaling (Eq. (2)) it follows that the isochoric steepness index,  $m_V$ ,<sup>3</sup>

$$m_V = \left. \frac{\partial \log(x)}{\partial (T_g/T)} \right|_{V=V_g} = \left. \frac{\partial \log(x)}{\partial (T_g V_g^\gamma / TV^\gamma)} \right|_{TV^\gamma = T_g V_g^\gamma} = const \quad (3)$$

and that  $m_V$  is related to  $m_p$  by<sup>3–5</sup>

$$m_p = m_V [1 + \gamma \alpha_p(T_g) T_g], \quad (4)$$

where  $\alpha_p(T_g)$  is the expansion coefficient at  $T_g$ .

One open question that remains in the literature is whether there is a relationship between the steepness

index of the dynamics  $m_p$  (or  $m_v$ ) and the shape of the potential. Results from dynamic measurements of colloids found that softer colloids make stronger glasses (i.e., having smaller  $m_p$ ).<sup>21</sup> This result, however, is in contrast with recent molecular dynamics simulations (done at constant volume) finding either an increase of  $m_v$  with increasing of the softness of the potential<sup>22,23</sup> or no appreciable change in  $m_v$ .<sup>24</sup> The comparison of the MD simulations is not easy since the used potentials are not exactly the same and it is not clear how this difference may influence the results (for example, differently from the more recent simulations in Ref. 21 where the potential was purely repulsive without any attractive term). Another limitation is that the dynamic range accessed by simulations is still quite far from the glass transition where the changes in  $m_v$  are generally smaller than close to  $T_g$ , therefore, changes in  $m_v$  are more difficult to assess if simulations are done in a more limited range.

The decrease of  $m_v$  with increasing of the softness of the potential from the colloidal systems is also in contrast with the observed decrease of  $m_v$  with increasing  $\gamma$  for dielectric relaxation data on supercooled liquids at high pressure.<sup>25</sup> Herein, we re-examine the method used to determine the steepness index in the dynamics of colloids and find that the observed behavior is not necessarily in contrast with an increase of  $m_v$  with increasing the softening of the potential and that actually the observed changes can be attributed mainly to the change of  $\gamma$ .

## II. RESULTS AND DISCUSSION

Colloidal systems are often used as a direct test of dynamic models since the large particle size permits the direct observation by optical techniques of both their structure and dynamics. Colloidal systems can be considered as quasi-ideal systems of interacting spheres, like in the work of Mattsson *et al.*,<sup>21</sup> wherein even the softness of the potential can be changed by changing the elastic properties of the particles.

Mattsson *et al.*<sup>21</sup> found very large differences in the behavior of the relaxation time versus concentration,  $\xi$ , with the stiffer particles having a much steeper dependence than softer particles (Figure 1). In this case the concentration is  $\xi = nV_0$ , where  $n$  is the number density of particles and  $V_0$  is the volume of an undeformed particle (that is constant). The number density is equal to the total number of particles  $N$  divided by the total volume  $V_{tot}$ ,  $n = N/V_{tot}$ . Therefore, these measurements in colloids are analogous to changing volume by applying pressure at constant temperature.

The behavior of the dynamics of supercooled liquids as a function of the  $T$  and  $V$  can be well described by the modified Avramov model<sup>26,27</sup>

$$\log \tau(T, V) = \log \tau_0 + \frac{A}{(TV)^\gamma}. \quad (5)$$

Equation (5) allows to extract the parameter  $\gamma$  from the best fit to the data. For the case of the colloids since  $T$  is constant, this equation reduces to

$$\log \tau(T, V) = \log \tau_0 + \tilde{A}\xi^{\gamma\phi}. \quad (6)$$

Fitting Eq. (6) to the data of Mattsson *et al.*<sup>21</sup> (Figure 1) we find that this equation well describes the data. Therefore,

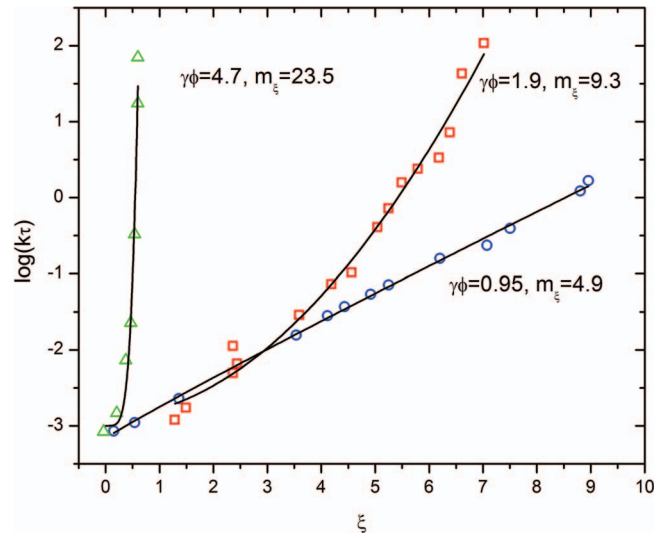


FIG. 1. Relaxation times versus concentration from Mattsson *et al.*<sup>21</sup> The triangles are for the stiffer particles, the circles for the softer particles, and the squares for the intermediate case. The three colloidal suspensions had particles with different elastic properties. The stiffer particles showed stronger dependence on  $\xi$ . The solid lines are the best fit using the modified Avramov equation. The values of  $m_\xi$  was calculated from the best fit as  $m_\xi = \gamma\phi(\log(\tau) - \log(\tau_0))$ .

the behavior of the dynamics in colloids can be described in the same framework as for supercooled liquids. We find that softer are the particles smaller is  $\gamma\phi$ , and this is what we expect since softer particles will give a softer potential and therefore a smaller value of  $\gamma$ . However, since the measurements were done only at a single  $T$  neither the value of  $\gamma$  or  $m_v$  can be determined from these data.

Since the measurements on the colloidal systems were done varying the concentration,  $\xi$ , at constant temperature, in this case the steepness index for the dynamics can be defined as

$$m_\xi = \left. \frac{\partial \log(\tau)}{\partial(\xi/\xi_g)} \right|_{\xi=\xi_g}. \quad (7)$$

Since  $\xi \sim 1/V$ , then

$$m_\xi = \left. \frac{\partial \log(\tau)}{\partial(V_g/V)} \right|_{V=V_g}. \quad (8)$$

It is important to note that the quantity  $m_\xi$  is quite different from  $m_p$  or  $m_v$  (Eqs. (1) and (3)) since the first describes the volume dependence of the dynamics while the latter are related to the temperature dependence of dynamics. Taking as example the relaxation times for several glass formers measured at different temperatures and pressure shown in Figure 2, the results show that the  $V$  and  $T$  dependences do not correlate, and that clearly the materials having the largest  $m_\xi$  are not the most fragile (i.e., having the largest  $m_p$ ).

By making use of the properties of partial derivatives it can be shown that

$$m_\xi = -\frac{1}{V_g} \left( \frac{\partial T}{\partial(1/V)} \right)_{\tau=\tau_g} \left( \frac{\partial \log \tau}{\partial T} \right)_{V=V_g}. \quad (9)$$

And using the definition of  $m_v$  (Eq. (3)) together with the thermodynamical scaling property (Eq. (2)) that for

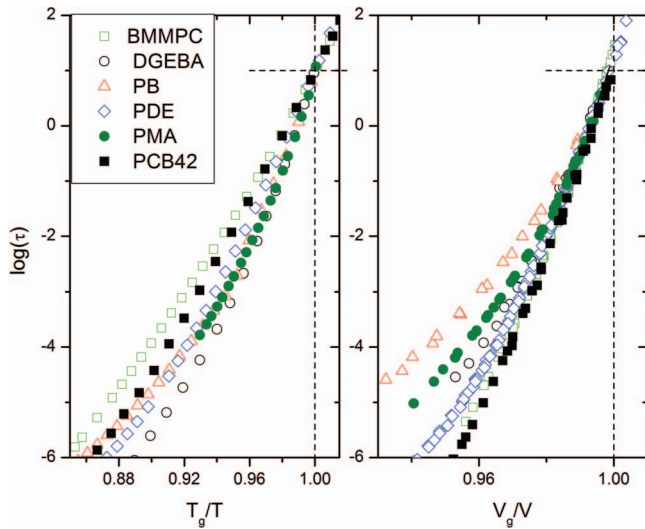


FIG. 2. Comparison of the steepness of the variation of the relaxation time with respect to the normalized temperature and to the normalized specific volume. There is no apparent correlation between the two behaviors.

$\tau = \tau_g \rightarrow TV^\gamma = T_g V_g^\gamma$ , we find

$$m_\xi = -\frac{1}{V_g} (T_g V_g^\gamma \gamma V^{1-\gamma})_{\tau_g} \left( -\frac{m_V}{T} \right)_{V_g} = \gamma m_V. \quad (10)$$

Therefore, even if  $m_\xi$  is related to  $m_V$ , since  $\gamma$  is not the same for the different colloids, larger  $m_\xi$  does not necessarily mean larger  $m_V$  as concluded by Mattsson *et al.*<sup>21,28</sup> Changing the elastic properties of the colloids is an effective way to change the repulsive part of the interparticle potential and we expect that the different colloids would have quite different  $\gamma$ , with softer particles having a smaller  $\gamma$  than stiffer particles. Thus, according to Eq. (10) the decrease of  $m_\xi$  for softer particles could be actually attributed to a decrease of  $\gamma$  without any change of  $m_V$ .

To investigate further the correlation between  $m_\xi$  and the isochoric fragility and  $\gamma$ , in Figure 3 we reported  $m_\xi$  for 24 glass formers versus the isochoric steepness index  $m_V$  (Figure 3(a)) and the scaling parameter  $\gamma$  (Figure 3(b)). The data in Figure 3(a) show that there is a lack of correlation between  $m_\xi$  and  $m_V$ , and in fact a linear fit (dotted line) gives a  $R^2$  close to zero indicative of no correlation. On the other hand, the data in Figure 3(b) show that  $m_\xi$  tends to increase with increasing  $\gamma$ , with a dependence that is more pronounced in the case of polymers than in the case of small molecules. Thus, for actual supercooled liquids, larger  $m_\xi$  are roughly associated more with larger  $\gamma$  than with larger  $m_V$  (or  $m_{p0}$ <sup>28</sup>), suggesting that this could be the case also for the colloidal systems.

In conclusion we have re-examined the dynamic relaxation data on colloidal systems investigated by Mattsson *et al.*<sup>21</sup> We confirm their results that the steepness index  $m_\xi$  decreases with the increasing softness of the potential. However, we show that an increase of  $m_\xi$  does not imply an increase of the fragility  $m_V$  (or  $m_{p0}$ <sup>28</sup>), especially because the expected increase of steepness of the potential,  $\gamma$ , alone would be enough to explain the observed increase of  $m_\xi$  (Eq. (10)). Dielectric relaxation results at high pressure on

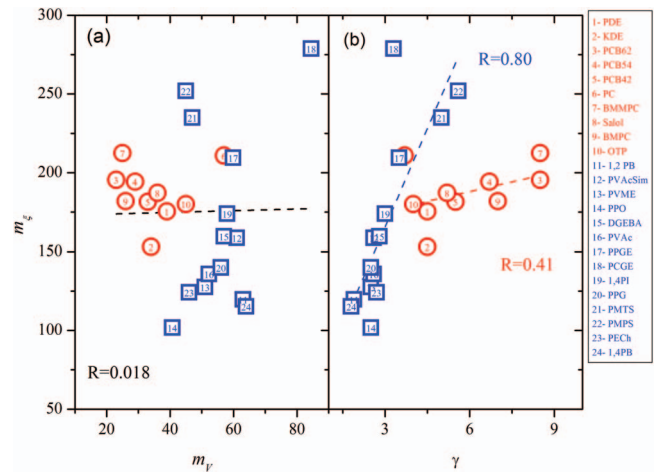


FIG. 3. The steepness index  $m_\xi$  versus the isochoric steepness index  $m_V$  (a) and the scaling parameter  $\gamma$  (b). The circles are small molecules and the squares are polymers. The data are from Ref. 25. The lines are the best linear fit to all the data in (a), and to the polymers and small molecules data separately in (b),  $R$  is the corresponding correlation coefficient.

glass forming liquids also show that the increase of  $m_\xi$  is more likely related to an increase of the exponent describing the steepness of the interparticle potential,  $\gamma$ , than to an increase of  $m_V$ . Measurements varying both concentration and temperature in colloids could help disentangle the effects of the softness of the potential on the fragility.

## ACKNOWLEDGMENTS

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- <sup>27</sup>R. Casalini and C. M. Roland, *J. Non-Cryst. Sol.* **353**, 3936 (2007).
- <sup>28</sup> $m_V$  has been found linearly correlated with  $m_{p_0}$  (Ref. 25), so that materials with the larger  $m_V$  are generally more fragile and *vice versa*.