LETTER TO THE EDITOR

Scaling in soft spheres: fragility invariance on the repulsive potential softness

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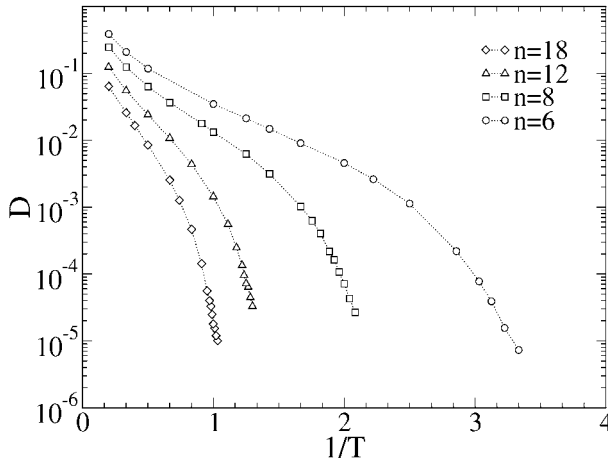
Abstract
We address the question of the dependence of the fragility of glass forming supercooled liquids on the 'softness' of an interacting potential by performing numerical simulation of a binary mixture of soft spheres with different power n of the interparticle repulsive potential. We show that the temperature dependence of the diffusion coefficients for various n collapses onto a universal curve, supporting the unexpected view that fragility is not related to the hard core repulsion. We also find that the configurational entropy correlates with the slowing down of the dynamics for all studied n.

When a liquid is cooled below its melting temperature, if crystallization does not take place, it becomes *supercooled*. In this supercooled region, the viscosity increases by more than 15 orders of magnitude in a small T-range. When the viscosity η reaches a value of about 10^{13} P the liquid can be treated as an amorphous solid, i.e. a glass [1–4] and the corresponding temperature is defined as the glass transition temperature (labelled T_g).

The T-dependence of the viscosity η differs for different glass formers. Angell has proposed a classification based on the behaviour of $\eta(T)$. Glasses are said to be *fragile* if they show large deviations from an Arrhenius law ($\eta(T) \propto \exp[E/T]$) or *strong* otherwise [5]. The fragility m of a glass forming liquid can be quantified by the slope of $\log \eta(T)$ versus T_g/T, evaluated at T_g, i.e. as

$$m = \frac{d \log \eta}{d(T_g/T)}\bigg|_{T=T_g}. \tag{1}$$

While the original definition of fragility is based on a purely dynamic quantity, correlation between m and other physical properties of glass forming liquids, both with dynamic and thermodynamic properties, have been reported. Recently, a correlation with vibrational properties of the glass state has also been reported [6]. One of the main challenges in the physics of supercooled liquid and glasses is to understand the connection between dynamical properties of the liquid close to the glass transition, i.e. the fragility, and microscopic properties.

Figure 1. T-dependence of the diffusion coefficient for all n investigated. D is measured in units $\sqrt{\sigma_{AA}^2 \epsilon_{AA}/M}$.

Is the fragility most affected by the steepness of the repulsive potential or by the interparticle attraction? Is it controlled by other properties of the interaction potential? In the present letter we address this question calculating numerically the fragility of several models for liquids, differing only in the softness of the repulsive potential. We aim at understanding whether changing the softness of the repulsive potential changes the fragility accordingly. We show more generally that the diffusion coefficient D can be scaled on a universal master curve by changing the softness of the repulsive potential. This implies that the fragility does not depend on the softness of the interaction potential. We complement this dynamical study with the evaluation of the configurational entropy to check the validity of the Adam–Gibbs [7–10] relation. In this letter we consider a simple glass former, a 80:20 binary mixture of $N = 1000$ soft spheres [11–13], which is an ensemble of spheres interacting via the following potential
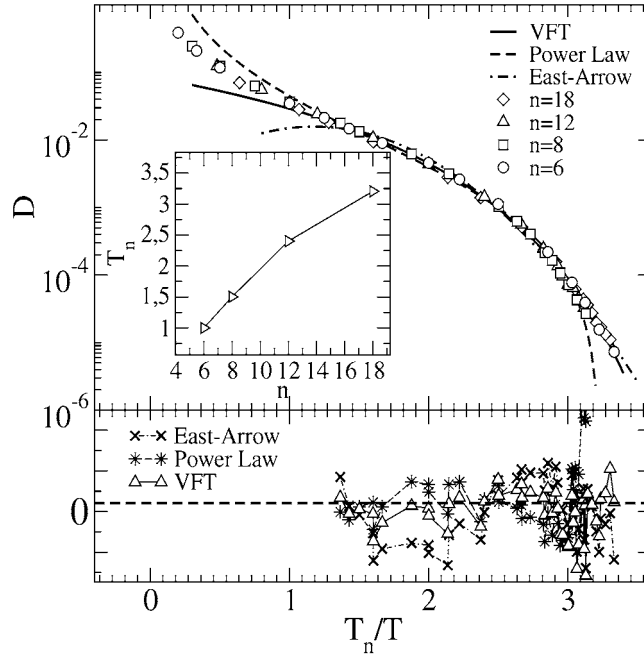
$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left(\frac{\sigma_{\alpha\beta}}{r}\right)^n \tag{2}$$

where $\alpha, \beta \in A, B$, $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, $\sigma_{BB} = 0.88$, $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$ and n is a parameter by which is possible to tune the 'softness' of the interaction [14]. This interaction potential is a Kob–Andersen potential [15] in which the attractive part of the potential has been dropped. In particular we investigate the values $n = 6, 8, 12, 18$.

This choice for the binary mixture is motivated by the fact that such a system is not prone to crystallization, that is it can be easily supercooled below its melting temperature. Still, for $n < 6$, crystallization takes place within the simulation time, determining a lower limit to the range of investigated n values. Reduced units will be used in the following, length will be in units of σ_{AA}, energy in units of ϵ_{AA} and time in units of $(M\sigma_{AA}^2/\epsilon_{AA})^{1/2}$, where M is the mass of all particles. In physical units, assuming the atom A is argon, the units are a length of 3.4 Å, an energy of 120 K k_B and a time of 2.15 ps.

At fixed n, the self-similar nature of the soft-sphere potential couples T and V. It can be shown that all thermodynamic properties depend on the quantity $TV^{n/3}$ [16]. Dynamic properties can also be scaled accordingly [17]. Hence, it is sufficient to quantify the T-dependence or the V-dependence of any observable to fully characterize the behaviour of the system. As a consequence the fragility does not change upon changing the density of the soft binary mixture, at fixed n.

Figure 1 shows the T-dependence of the diffusion coefficients, evaluated from the long time limit behaviour of the mean square displacement, for all n investigated and covering a

Figure 2. Master curve for diffusion coefficient D calculated rescaling the temperature by an n-dependent quantity. Full curve is a Vogel–Fulcher–Tamman fit to all points lying in the landscape-influenced region [20, 21], which for the present model corresponds to $\xi < 0.78$ with $\xi = T/T_n$, i.e. $\mathcal{D}(\xi) = A\exp[B/(\xi - \xi_0)]$. The fitting parameters $\ln A$, B and ξ_0 are, respectively, -2.46, -0.857 and 0.209. From this master curve one can also estimate the dynamic fragility, which is about 130.4. The dashed curve is a fit to all points lying in the interval $0.328 < \xi < 0.833$, to a power law [22–24], i.e. $\mathcal{D}(\xi) = A_m(\xi - \xi_c)^\gamma$, where $\ln A_m = -2.41$, $\xi_c = 0.309$, $\gamma = 1.88$. The dot–dashed curve is a fit to $D(\xi) = \exp(A_0\xi^2 + A_1\xi + A_2)$, according to [25]. The fitting parameters A_0, A_1, A_2 for the latter case are, respectively, -1.61, 3.79, -6.38. The inset shows the n-dependence of the scaling parameter T_n. The bottom part shows the error of all three fitting functions ($\ln D_{\text{data}} - \ln D_{\text{fit}}$).

window of about four orders of magnitude. At high T the behaviour is consistent with the quasi-universal behaviour proposed by Rosenfeld [18]. In the attempt to compare the n-dependence of the diffusion coefficient, we report in figure 2 the data as a function of T_n/T, where T_n is chosen in such a way to maximize the overlap between data of different n, i.e. to collapse all data onto a single master curve. Figure 2 shows that all curves can be successfully scaled onto the master curve $\mathcal{D}$ choosing a proper set of scaling parameters T_n (whose n-dependence is plotted in the inset of this figure). The very good quality of the resulting master curve

$$D(T) = \mathcal{D}(T/T_n) \tag{3}$$

suggests that the n-dependence enters only via a rescaling of the temperature[3,4]. The remarkable consequence of the latter result is that the fragility of the system does not depend on the repulsive interaction potential. In fact according to equation (3) and from the definition

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[3] Note that linear extrapolation of T_n with n shows that T_n goes to 0 at same value $n \simeq 2$. This may suggest that below a critical value of the range of the potential the T-dependence of the diffusivity coefficients exhibits a strong crossover to a different regime. Below this critical value the T-dependence of the diffusion coefficient should be weak.

[4] The scaling behaviour of the temperature dependence of the diffusion coefficients on varying the density for ortho-terphenyl has been studied in [19].

of the liquid's fragility m given in equation (1), assuming $D \propto \eta^{-1}$, we get:

$$m = \frac{T_g(n)}{T_n} \frac{1}{\mathcal{D}[T_g(n)/T_n]} \frac{d\mathcal{D}(x)}{dx}\bigg|_{x=T_g(n)/T_n} \tag{4}$$

where $T_g(n)$ is the glass transition temperature for the system with softness n, which can be defined as the temperature at which diffusivity reaches an arbitrary small value $10^{\mathcal{K}}$,[5] i.e.

$$-\log D[T_g(n)] = -\log \mathcal{D}\left[\frac{T_g(n)}{T_n}\right] = \mathcal{K}. \tag{5}$$

Equation (4) shows that the fragility index m is a function only of the scaled variable $\frac{T_g(n)}{T_n}$ and hence, as far as the scaling reported in figure 2 keeps holding even at temperatures lower than the one we are able to equilibrate, the dynamic fragility m is independent of n as well. By fitting the master curve to a Vogel–Fulcher–Tamman (VFT) fit, as shown in figure 2, an estimate of $\frac{T_g(n)}{T_n} = 10^{\mathcal{K}}$ can be calculated, resulting into a estimation of $m \approx 130$. This figure should be compared with the value $m = 81$ for o-terphenyl (OTP), which is a typical fragile liquid and $m = 20$ for the prototypical strong glass the liquid silica (SiO_2).

For completeness, we report also in figure 2 a fit of the master curve according to the prediction of mode-coupling theory (MCT), which has been shown to be consistent with numerical data for several models in the weak supercooled region. A best fit procedure requires the exclusion of the low T points, for which deviations from the power-law fit are observed[6]. We also show for completeness a fit to the functional form proposed by kinetically facilitated models [25]. Figure 2-bottom shows the errors of all three fit functions.

Recently, evidence has been presented that kinetic fragility strongly correlates with thermodynamic fragility [26]. In this respect, it is worth looking if the scaling observed in dynamic properties has a counterpart in thermodynamic properties. In particular, we evaluate the configurational entropy for the system, within the potential energy landscape framework as discussed in detail in [27–32]. In brief, we estimate S_c as difference between the liquid entropy (calculated via thermodynamic integration from the ideal gas) and of the vibrational entropy (calculated via thermodynamic integration, including anharmonic corrections, from the very low temperature harmonic dynamics of the disordered solid associated to the liquid configuration). We then focus on the ability of the Adam–Gibbs (AG) relation, which states that

$$D(T) = A_{\mathrm{AG}} e^{\frac{B_{\mathrm{AG}}}{T S_c}}, \tag{6}$$

to model the temperature dependence of D. Figure 3 shows the AG plot for the studied n values. For all n, a satisfactory linear representation of $\log(D)$ versus $1/T S_c(T)$ is observed. As discussed in more detail in [33], the simultaneous validity of the VFT description of D and of the AG relation requires the identity of the kinetic and thermodynamic fragilities. In this respect, the independence of n discussed above for the case of kinetic fragility carries on also to thermodynamic fragility.
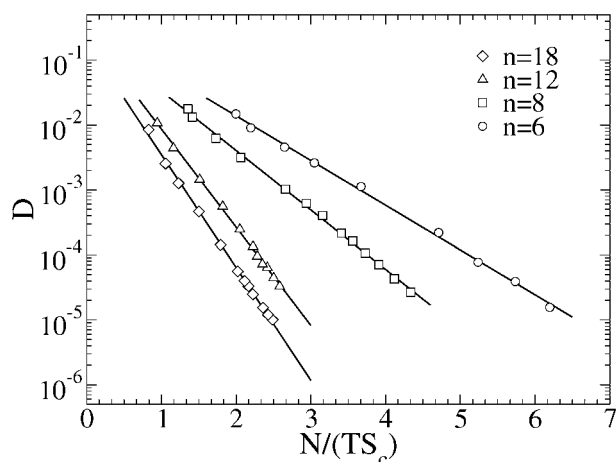
A remarkable consequence of the validity of the AG relation (equation (6)), associated to the scaling with n of D (equation (3)) is that the configurational entropy can be written as

$$S_c(T) = S_0(n)\mathcal{F}(T/T_n) \tag{7}$$

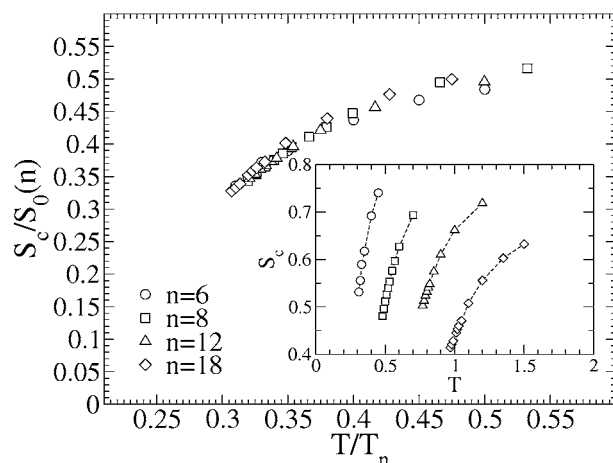where $F(x)$ is a scaling function and $S_0(n) = B_{\mathrm{AG}}/T_n$. To support such a proposition, we show in figure 4 S_c multiplied by the factor B_{AG}/T_n as a function of T/T_n, where T_n are the

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[5] In particular we have made the choice $D[T_g(n)] = 10^{\mathcal{K}} = 5.75 \times 10^{-16}$, this value for the diffusion coefficient ensures that at T_g the relaxation time is about 100 s.

[6] We also note that a Bassler form ($D(\xi) = A\exp(B/\xi^2)$) does not reproduce the data in a manner comparable to VFT and MCT.

Figure 3. Test of the Adam–Gibbs relation based on the configurational entropy values calculated subtracting the anharmonic and harmonic entropies from the total entropy (see [27] for details). The fitting parameters $\ln A_{AG}$ and B_{AG} are: for $n = 6$, -1.112, -1.584; for $n = 8$, -1.303, -2.105; for $n = 12$, -1.271, -3.481; for $n = 18$, -1.657, -4.002. TS_c is measured in units of ϵ_{AA}.

Figure 4. Master plot of the configurational entropy (see equation (7)). The inset shows the temperature dependence of the configurational entropy.

values for which D scaling is recovered (inset of figure 2). Again, the quality of the data collapse stresses the validity of the scaling with n.

To conclude, the relevant result that has been shown in this letter is that in the case of soft sphere potentials, the dynamic fragility is independent of the power n of the short range repulsion. This conclusion is based on the hypothesis that the scaling observed in the range of T where simulations are feasible extends also to lower temperatures, down to the glass transition temperature. Indeed, a particular effort has been made to equilibrate configurations to temperatures lower than the MCT temperature, where dynamical processes different from the ones captured by MCT are active. If the scaling is indeed valid, the results presented in this letter strongly support the possibility that, contrary to our common understanding, fragility in liquids is mostly controlled by other properties of the potential, more than by the hard core

repulsion. This suggests that the attractive part of the interaction as well as the non-sphericity of the interaction must intervene in the determination of the system fragility. Finally we note that one could be tempted to associate the fact that the diffusion coefficient data can be rescaled only by changing the energy scale by T_n to a simple overall rescaling of the landscape potential. The data in figure 4 suggest that this is not the case since $S_c(E)$ is not just a scaling function of T/T_n but it needs to be rescaled by a factor $S_0(n)$ and hence the number of distinct basins explored at the same T/T_n changes with n. A non-trivial compensation mechanism between the scaling of the static properties (S_c) and the scaling of the kinetic coefficient $B_{AG}(n)$ (defined in equation (6)) on n must be present.

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