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Silica through the eyes of colloidal models—when glass is a gel

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Abstract
We perform molecular dynamics simulations of ‘floating bond’ (FB) models of network-forming liquids and compare the structure and dynamics against the BKS model of silica (van Beest et al 1990 Phys. Rev. Lett. 64 1955), with the aim of gaining a better understanding of glassy silica in terms of the variety of non-ergodic states seen in colloids. At low densities, all the models form tetrahedral networks. At higher densities, tailoring the FB model to allow a higher number of bonds does not capture the structure seen in BKS. Upon rescaling the time and length in order to compare mean squared displacements between models, we find that there are significant differences in the temperature dependence of the diffusion coefficient at high density. Additionally, the FB models show a greater range in variability in the behavior of the non-ergodicity parameter and caging length, quantities used to distinguish colloidal gels and glasses. Hence, we find that the glassy behavior of BKS silica can be interpreted as a ‘gel’ at low densities, with only a marginal gel-to-glass crossover at higher densities.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, researchers have introduced simplified models to better understand the essential elements behind the unconventional thermodynamic and dynamic properties of silica, water and tetrahedral network-forming liquids in general, as well as the differences between them, such as why silica is such a good glass-former, while water readily crystallizes. Compared to atomistic models such as the BKS model of silica [1] and the SPC/E model for water [2], these simpler models condense the long-range electrostatic interactions into short-range ones but, following the pioneering work of Kolafa and Nezbeda on water [3], explicitly enforce a tetrahedral valence by decorating hard spheres with four sticky spots for water or one-component tetrahedral particles [3–5], or by employing a 1:2 mixture of spheres with four and two sticky spots representing Si and O atoms in silica [6, 7].

Interestingly, these types of simpler models have recently become relevant for colloidal systems, especially in the framework of newly synthesized patchy particles [8–11] or for functionalized particles, either via DNA-binding [12–14] or through specific attraction [15, 16]. Networks can also be studied by simulating binary mixtures of particles interacting with isotropic interactions, where one species provides the network nodes and the other one acts as a collection of ‘floating bonds’ (FBs) [17–20]. Tetrahedrality is attained by stoichiometry and a judicious choice of the potential parameters, and could potentially be achieved experimentally with mixtures of oppositely charged particles [21].

Recently, it was noticed that generic four-valence models, including primitive models of water [3] and silica [6], DNA dendrimers [12], the limited valency model [22, 23], as well as the FB model [18, 19], share a similar phase diagram [24] both in terms of the location of the gas–liquid spinodal and in the behavior of the iso-diffusivity lines, once temperature and density are correctly scaled respectively to the critical temperature and to the number density of network nodes. This phase diagram was also compared to those of well-studied models of water (SPC/E and ST2) as well as to BKS silica, again showing striking similarities [24]. Building on this
correspondence, we provide in this article a direct comparison between the more realistic and well-studied model for silica—the BKS model—and two simpler FB models, mimicking tetrahedral-forming colloidal particles.

The BKS model consists of short-range pairwise additive forces along with long-range Coulomb interactions, and reproduces to varying degrees of accuracy the physical properties of silica we are seeking to understand with (short-range) FB models. While the coefficients used in the BKS potential can be refined to improve its comparison with experiments [25, 26] (indeed BKS is an improvement over the TTAM potential [27]) and further improvements can be achieved through adding three-body forces and variable charges [28], the BKS model has become a standard for computational studies of the static and dynamic properties of silica [29, 30], and serves as a point of comparison for further improvements [31]. Modifications to BKS-like potentials have shed insight into the physics of the network-forming liquids MX₂, such as was done in [32], in which the authors detail in [18], is based on (non-additive) hard-core repulsions which the bonds can form reversibly and have a finite lifetime.

character, we are studying them at a temperature scale for gels [37], where the bond strength is of the order of the gel and a (fragile) glass [24, 40].

Interesting to connect this transition to that between a (strong) silica [29, 30], and serves as a point of comparison for further computational studies of the static and dynamic properties of charges [28], the BKS model has become a standard for be achieved through adding three-body forces and variable the TTAM potential [27]) and further improvements can interactions.

(a mixture), rather than to a system with explicit three-body particles (modeling Si atoms, labeled 1) that interact with each other via a hard sphere interaction of diameter σ, and 2000 ‘floating bonds’ (O atoms, labeled 2). For both FBH and FB, particles of types 1 and 2 interact through a short-range square well

\[ V_{12}(r) = \begin{cases} \infty & r < \sigma_{12} \\ -\mu_0 & \sigma_{12} < r < \sigma_{12} + \delta \\ 0 & r > \sigma_{12} + \delta \end{cases} \] (1)

where \( \sigma_{12} = 0.55\sigma \), and \( \delta/(1 + \delta) = 0.03\sigma_{12} \). For FBH, type 2 particles interact with a hard sphere repulsion of diameter \( \sigma_{22} = 0.8\sigma \). For FB, the potential between particles of type 2 is softened to a finite shoulder via

\[ V_{22}^S(r) = \begin{cases} \infty & r < \sigma_{\text{small}} \\ \mu_0 & \sigma_{\text{small}} < r < \sigma_{22} \\ 0 & r > \sigma_{22} \end{cases} \] (2)

where \( \sigma_{\text{small}} = 0.1\sigma \). Both types of particle have mass \( m \). The FBH and FB models are studied by extensive event-driven molecular dynamics simulations.

A detailed comparison between BKS and the FB models requires a mapping of the length and time scales. In the following we use the network node–node distance \( \sigma_{\text{eff}} \) (the equivalent of the Si–Si distance in BKS), taken to be the location of the first peak in the Si–Si partial radial distribution function, as a unit of length. For BKS, \( \sigma_{\text{eff}} = 0.31 \text{ nm} \) and for the FB models \( \sigma_{\text{eff}} = 1.05\sigma \). With this unit, the scaled number densities \( \rho^* = N_p \sigma_{\text{eff}}^3/V \) (again, \( N_p \) is the number of node (Si) particles and \( V \) is the volume) for the BKS isochores are \( \rho_{\text{low}} = 0.69 \) and \( \rho_{\text{high}} = 1.16 \). We also scale time by \( t_{\text{eff}} \), the approximate time at which the ballistic motion of the node atoms crosses to diffusive motion. For BKS

2. Models and simulations

The FBH model was initially studied in [18, 19]. The FB model, introduced here, also consists of \( N_p = 1000 \) ‘node’ particles (modeling Si atoms, labeled 1) that interact with each other via a hard sphere interaction of diameter \( \sigma \), and 2000 ‘floating bonds’ (O atoms, labeled 2). For both FBH and FB, particles of types 1 and 2 interact through a short-range square well

\[ V_{12}(r) = \begin{cases} \infty & r < \sigma_{12} \\ -\mu_0 & \sigma_{12} < r < \sigma_{12} + \delta \\ 0 & r > \sigma_{12} + \delta \end{cases} \] (1)

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silica, this corresponds to $t_{\text{eff}} = 75$ fs. For the FB models, $t_{\text{eff}} = \sigma \sqrt{m/\mu_0}$, i.e. simply the usual definition of unit time. The temperature for the FB models is reported in reduced units, $T^* = k_B T/\mu_0$.

In order to compare the structure and dynamics, we report the following quantities: the static structure factor $S(q)$, the mean square displacement (MSD) of node particles along with its associated caging length $l_0$, defined as the square root of the height of the MSD plateau prior to the onset of diffusive behavior; the non-ergodicity parameter $f_q$ and stretching exponent $\beta_q$, both of which are obtained from a fit of the secondary relaxation portion of the intermediate scattering function $F(q, t) = \rho_q(t) \rho_q(0) / S(q)$ to the fitting function $f_q \exp\left[-(t/t_0)^\beta_q\right]$. All quantities are based on node particles alone, Si atoms in the case of BKS silica and the larger particles in the FBH and FBS systems.

### 3. Results

In figure 1(a) we compare $S(q)$ for low $T$ and low density for BKS and FBH. At low density, $S(q)$ for FBS is not discernible from FBH, and is therefore not shown. The pre-peak in $S(q)$ displayed by BKS silica at $\rho_0^{*}$ is a signature of the developed tetrahedral network. It is also found in the FB models at $\rho^* = 0.66$, with a slightly lower intensity. Hence in terms of static structure, there seems to be quite a good correspondence between the models (also in terms of $\rho^*$).

At higher density the situation is different, as illustrated in figure 1(b). Now the BKS structure is very different from that of either FBH or FBS near comparable densities. Indeed, the splitting of the first $S(q)$ peak in BKS persists up to high density despite six-fold coordination, suggesting the presence of a locally ordered octahedral network. On the other hand, in the FB models, geometrical preference is lost with increasing density, even in the case of FBS, where the model would allow for the formation of six bonds per particle.

To compare the FB and BKS dynamics, we begin by finding state points in FBS and FBH that match the mean square displacement of BKS at the lowest $T$ for both isochores, both in terms of diffusion coefficient and plateau height. In figure 2(a), we see that for $\rho_0^{*}$ at $T = 3000$ K, the MSD is matched by both FBH and FBS at $(\rho^*, T^*) = (0.88, 0.10)$ (a density considerably larger than $\rho_0^{*}$), while for $\rho_{\text{high}}^{*}$ at $T = 2400$ K, the MSD is matched by FBH at $(\rho^*, T^*) = (1.05, 0.15)$, and by FBS at $(1.15, 0.15)$. This matching procedure operated at the lowest BKS studied temperature provides us with a conversion value to compare the full $T$-dependence of the dynamics in the different models. It is found that such a procedure implicitly assumes a conversion factor for $T$ which is density dependent, providing the scaling factors $T_B = 3000/0.1$ at $\rho_0^{*}$ and $T_B = 2400/0.15$ at $\rho_{\text{high}}^{*}$.

In this way, we report in figure 2(b) the $T$ dependence of the self-diffusion coefficient $D$, evaluated from the long time limit of the MSD, normalized by $\sigma_{\text{eff}}^2/\mu_0$. The FB models at $\rho^* = 0.88$, at low $T$, match the $\rho_0^{*}$ BKS isochore quite well, being nearly parallel for more than two orders of magnitude in $D$. For the $\rho_{\text{high}}^{*}$, BKS isochore, the agreement with the FB models is worse. While in BKS the $T$-dependence of $D$ is non-Arrhenius, $D$ for the FB models shows a clear Arrhenius dependence at low $T$. The two FB models show fairly good agreement with each other.

Figure 3 shows the caging length as a function of density along the isotherms $T = 3000$ K for BKS and $T^* = 0.10$ for the FB models. It is evident that $\rho^* \approx 0.88$ marks the threshold above which the two FB models become different. Above this value, the soft-core interactions enter into play as the packing increases, although, as we have seen in figure 1, the structures remain quite similar. It is quite clear that for similar changes in density, BKS shows much less change in $l_0$ than the FB models. The similarity between FBH and FBS is highlighted in the inset of figure 3, where we show the pressure dependence of $l_0$. While the two FB curves collapse, BKS shows a strong departure. Here, in order to compare the models, we have reduced the pressures by a factor $m_{\text{Si}}/T_0^2 \sigma_{\text{eff}}^2$, which is $2.68 \times 10^{10}$ Pa for silica. We note that the BKS model exhibits negative pressures for densities near $\rho_0$ at $3000$ K—a drawback that can be addressed by reparameterizing the potential [25, 26].

We now try to gain a deeper understanding of the nature of the dynamical arrest occurring at different densities, viewing silica through the eyes of colloidal systems. Indeed, as alluded to in the beginning, the FB models could perhaps be realized with colloidal particles. The behavior of $l_0$, extracted from the MSD, already indicates an increasing length scale associated with arrest as the density decreases. To better characterize the underlying arrest mechanisms in terms of the different length scales, it is instructive to monitor the so-called non-ergodicity parameter $f_q$, i.e. the plateau height of the collective density correlation function. This typically oscillates in phase with $S(q)$ and is non-zero in a finite range of $q$, providing direct evidence of the characteristic length scales over which the system becomes non-ergodic. While for a standard glass $f_q$...
is significantly different from zero at all physically relevant q-values, implying that all length scales are arrested, gels exhibit a very different behavior [22, 44]. Indeed, $fq$ is finite only at small $q$, providing evidence that only large length scales, typically of the order of the mesh of the gel network, are arrested, while on smaller scales (including nearest-neighbor ones) the system remains ergodic. Previous studies have also shown that, with increasing density, a gel-to-glass crossover is observed, signaled by a growth of $fq$ at all $q$ [40].

We now ask whether we can classify arrested states of silica as gel or glass by comparing the behavior of $fq$ to that of the FB models. We also monitor the behavior of the stretching exponents $\beta_q$. Colloidal gels can be viewed [24] as the counterpart of strong glasses ($\beta_q$ nearer to 1) [45], while colloidal glasses are similar to fragile glasses ($\beta_q$ smaller than 1).

Figure 4 shows $fq$ for state points that match the MSD in BKS, FBS and FBH (the same as in figure 2(a)). We see that for both $\rho_{\text{low}}^*$ and $\rho_{\text{high}}^*$, a match in the MSD corresponds also to a match in terms of $fq$ and $\beta_q$. Also shown in figure 4 are $fq$ curves for FBH at $\rho^* = 0.66$ and 1.15, in order to underline the dramatic variation in the range of $fq$ over a similar range in density as chosen for BKS. These two curves illustrate the signatures of gels and glasses in terms of $fq$. The softening of the non-additive repulsion between floating bonds in FBS reduces the extent of $fq$ to that seen in BKS at a comparably high density. As the density is lowered, BKS does not achieve the same degree of narrowing of $fq$ as the FB models. Thus we can conclude from figure 4 that if we can associate a narrow $fq$ with gels and an extended one with repulsive glasses, the ‘gel-to-glass’ crossover is much more muted in BKS. However, using FBS does shift the colloidal model toward the behavior of BKS.
4. Discussion

In the present paper, we compare BKS silica and two floating bond models, one that maintains tetravalent bonding to high densities (FBH) and one that allows more bonds to form as the density increases (FBS). The modifications present in FBS only seem to matter beyond $\rho^* = 0.88$; at lower $\rho^*$ the two models are practically the same.

At comparably low reduced number densities, $\rho_{\text{low}}^* = 0.69$ for BKS and $\rho_{\text{low}}^* = 0.66$ for both FBS and FBH, tetrahedral order is present in all models. However, in terms of dynamics, as shown by the caging length and the shape of the MSD, order is present in all models. However, in terms of dynamics, models are practically the same.

The stretching exponent $\beta_q$ exhibit a reduced density dependence of these quantities. A step toward a better understanding of this difference, FBS does glasses have a short $l_0$ along a curve of $\rho^*$, a large range of $f_q$ and $\beta_q$ closer to $1/2$. We find that while BKS does have a gel-to-repulsive glass trend, at least in terms of the range of $q$, the behaviors of $l_0$ and $f_q$ are much less dependent on density than in colloidal systems. As a first step toward a better understanding of this difference, FBS does exhibit a reduced density dependence of these quantities.

5. Conclusions

In this paper, we have exploited the similarity of the phase diagrams for generic tetrahedral models [24] in order to connect silica to simpler models relevant to colloidal systems. Working with reduced quantities, we find that the structure of the FB models maps fairly well to that of BKS at low density. However, there seems to be a mismatch in the density at which the dynamics are most similar.

The trend in the dynamics for BKS in going from low to high density is suggestive of the crossover from gel-to-repulsive glass seen in colloidal models, i.e. $f_q$ broadens in its extent, $\beta_q$ decreases although $l_0$ remains rather constant. However, the trend is not striking considering the behavior FBH and FBS exhibit over a similar range in $\rho^*$. While replacing the hard sphere repulsion with a shoulder in the FB model does not lead to anomalous behavior in density or diffusivity, it does change the dynamics (and the pressure) beyond $\rho^* \approx 0.88$ significantly, while only subtly changing the structure. The reduced pinning of tetrahedral centers provided by the shoulder brings FBS closer to the dynamical behavior of BKS, even though the splitting of the first peak in $S(q)$ is lost. The non-Arrhenius behavior of $D$ for BKS suggests a still-changing energy landscape at low $T$, particularly at $\rho_{\text{high}}^*$ which could be better captured by even softer FB models.

It would be interesting to know to what extent the lack of strong gel-to-glass signatures and the appearance of non-Arrhenius dynamics can be captured by models with short-range interactions, or whether longer-range forces are necessary.

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