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Chapter 6.1

Comparison of Pair-Potential Models for the Simulation of Liquid SiO₂: Thermodynamic, Angular-Distribution, and Diffusional Properties

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We extend a recent comparison of the abilities of different pair-potential models for SiO₂ to reproduce the IR spectrum of the glassy state (a short-time dynamic property) to other properties. The comparison is extended to include static (thermodynamic and structural) and long-time dynamic (diffusivity) properties. As with the IR spectrum, none of the existing potentials succeeds in correctly locating the temperature of the density maximum $T_{\rho(\text{max})}$. Although the modified Matsui potential, which best represented the IR spectrum, also performs well in describing $T_{\rho(\text{max})}$ and the intertetrahedral bond angle, it seriously overestimates the diffusivity and hence incorrectly represents the shape of the potential far from the minimum. The best performance across the range of properties examined is obtained with the van Beest–Kramer–van Santen potential. Some evidence for a higher-order phase transition below the density maximum is given.

6.1.1 Introduction

It is now two decades since it was found (unexpectedly to many) that key properties of liquid and glassy SiO₂ could be reproduced semiquantitatively by molecular-dynamics (MD) computer simulations in which the Si and the O components are treated as simple ions with full formal charges [1]. The internal energy at 300 K was obtained to within 3%, and the qualitatively unique features of (1) high liquid compressibility contrasting with low liquid expansivity, (2) anomalous increase of diffusivity with pressure, and (3) large pressure-induced glass densification were also demonstrated. The same simple two term potentials (now called TRIM, for transferable rigid-ion model, potentials

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because only one parameter, $\sigma$, is used to distinguish between different cations in oxide glass formers) also predicted correctly that it would not be possible to retain Si in six coordination on decompression from the six-coordinated state, regardless of whether the compression was carried out in the liquid or the glassy state [1, 2]. These simple transferable potentials, of the form

$$U(r) = z_i z_j / r + A_{ij} \exp[(\sigma_i + \sigma_j - r)/\rho],$$

(6.1.1)

have been very useful for establishing qualitative trends in the behavior of liquid and glassy silicates across a wide range of multicomponent systems [3–5], and for obtaining insight into structure–property relations in nonoxide glasses as well [6], although they are too simple to give quantitative predictions.

Professor Matsui was one of the first to recognize the possibilities of such simulation studies for solving geophysical problems, and his 1980 study of liquid MgSiO$_3$ [7] did much to awaken the geoscience community to what has now become a major field of activity [8]. He has also been very instrumental in the development of more accurate potential functions for use in these simulations, although, as will be seen, the provision of a quantitatively valid pair-potential model for SiO$_2$ is still an unfulfilled need.

A good example of the qualitative success but quantitative failure of the simple transferable potentials is provided by the unusual behavior of the density with varying temperature to which we devote considerable attention in this chapter. Maxima in density with varying temperature are very rare among liquids. The famous case of water at 4°C is often regarded as unique. However, it is also encountered in liquid SiO$_2$, not far above $T_g$, at 1820 K [9]. The existence of a density maximum in SiO$_2$ is qualitatively verified with the TRIM potential. However, the temperature at which the maximum occurs, 7–9000 K [10–12], is far higher than that observed in the laboratory material. Another failure of the simple model concerns the crystal state. The prediction of distinct polymorphs existing at different pressures and temperatures is an essential requirement of a good set of pair potentials – and is one that is not met by TRIM potentials. Accordingly, a variety of more accurate, but of course more complicated, potentials have been developed, of which the potential developed by Matsui and co-workers, the so-called Tsuneyuki potential [13], is a leading example.

Pair potentials that have been developed for the accurate evaluation of crystal-phase properties of SiO$_2$ have proven useful for the study of certain liquid- and glassy-state properties of this important substance, although they may be unsuitable for others. For instance, the Tsuneyuki potential, which was developed to describe the crystals [13] and was applied with apparent success to the calculation of glassy-state properties by Della Valle and Andersen [14], proves unsatisfactory for the calculation of the liquid-state diffusivities, which are some 3 orders of magnitude higher than expected from the measured viscosities (vide infra). In this latter respect, the Tsuneyuki potential is considerably less satisfactory than the simple TRIM potential. Indeed, there are some properties that none of the pair potentials yet developed appear capable of reproducing satisfactorily. We recently [15] documented the failure of all available pair potentials to reproduce the separation of the principal peaks of the IR spectrum. We now document
the failure of all available pair potentials to reproduce accurately the temperature of the density maximum, a liquid-state anomaly that is known from aqueous studies to be closely related to the anomalous pressure coefficient of the fluidity; hence it is of major geophysical importance [16, 17].

In the case of the IR spectrum, the addition of the many-body (i.e., non-pairwise-additive) interaction, arising from the polarizability of the oxide ion, was found necessary to obtain a correct description [18]. A variety of three-body (non-pairwise-additive) potentials have been developed [19–23] to improve the modeling of properties such as the average bond angle Si–O–Si, which in turn seems to be related to the IR band separation problem. Whether or not calculations with three-body potentials are more economic than the algorithms by which oxide-ion polarization is currently [18] being accounted for is not clear, but the latter approach is simpler and more satisfactory in principle. Ultimately it will be necessary to use the more fundamental Car–Parrinello approach [24] in which the forces acting on the atoms are evaluated at each step by high-order quantum-mechanical calculations, and the accelerations, hence the trajectories, are evaluated by the normal classical mechanical methods. The first applications of this approach to the simulation of SiO₂ have recently been reported [25]. Unfortunately, the computer time consumed in such simulations is so great that at this time they may be applied to only a very limited range of problems.

The last-mentioned ab initio calculations are for some purposes not helpful. There are many problems of fundamental as well as geophysical interest for which the ability to follow the system evolution over very many (preferably of the order of 10⁶) particle oscillations is essential. For such problems, which are on the border between class A and class B simulation problems [26], the use of pairwise-additive potentials is mandatory, given present computing speeds and algorithms. By way of example, a general problem for fragile supercooling liquids is that of establishing the physics of the bifurcation of the relaxation function into α and (slow)β processes. This is found to occur at a temperature that is very near the mode-coupling-theory critical temperature and at characteristic times that are some 3 orders of magnitude beyond the range of present computing capabilities. For the particular case of SiO₂ there is a more immediate problem. It is the problem of understanding the discrepancy (vide infra) between the diffusivity and the thermodynamic behavior of the best pair potentials (namely a strongly non-Arrhenius diffusivity coupled with − and expected from Ref. [27] − a considerable excess heat capacity [5, 28]) and that which is observed in the laboratory (an Arrhenius diffusivity and a very small excess heat capacity). We need to know whether the discrepancy has the same structural/geometrical origin as the anomalies seen in the simulation of H₂O by use of the best pair potentials. In the H₂O case there is a crossover from fragile liquid to strong liquid behavior during cooling. At ambient pressure such a transition might occur by means of a continuous transition [29–31] or (as in the case of liquid Si [32, 33]) by a first-order transition.

Thus there is a real need to evaluate the different pair potentials proposed for SiO₂ in order to determine how best to invest the considerable resources of computer time that will be necessary to resolve the above types of problem. In this chapter
we therefore extend our previous comparative study of the IR spectrum, a short-time dynamic property, to the study of static (thermodynamic) anomalies on the one hand and long-time dynamic properties on the other. In our earlier paper [15], we stressed how insensitive the gross structural characteristics of the glass (and liquid), such as the radial distribution functions (RDFs), are to differences in the pair potentials that were found to produce large differences in the IR spectrum. Here we will compare a different structural property, the Si–O–Si bond-angle distribution, which will be seen to be rather more sensitive than the RDF. However, it is the diffusivity, a long-time dynamic property, that proves, not surprisingly [15, 34], to be the most sensitive of all the properties studied to these differences in potential function.

6.1.2 Procedures

In the previous paper [15] we provided, in tabular form, the parameters of the pair potentials being compared. We cast all potentials in the same form to help identify where the essential differences lie. We do not repeat the tabulation here but note the origins of the potentials being compared. They are, in order of their appearance in the literature, (1) the TRIM potential, (2) the Kubicki–Lasaga potential [35], (3) the Tsuneyuki potential [9], (4) the van Beest–Kramer–van Santen (BKS) potential [36], and (5) the modified Matsui potential [15, 37]. There have been minor variations of the TRIM potential, of which we have used the version studied in detail by Poole et al [12]. There are also different implementations of the BKS potential (of which we have used the original version without the truncation adopted by Vollmayr et al. [28]). The modified Matsui potential, which gave the best representation of the IR spectrum [15], is a potential adapted by us from the potential devised by Matsui [37] for the simulation of a binary silicate. It is closely related to the Tsuneyuki potential but differs in the short-range attractive component and is more stable at high temperatures against the collapse that occurs easily in the Tsuneyuki (and also BKS) potential because of the vanishing of repulsive forces between particles on close approach [38].

The emphasis in this chapter, except for the bond-angle distribution, is on the behavior of the simulated system in the ergodic state, i.e., in states that are liquid on the computational time scale. Runs were carried out by stepwise cooling of a 450-ion system with periodic boundary conditions at fixed density. The density chosen was 2.20 g/cm³, that of the laboratory material that is almost independent of temperature up to 2000 K [9].

Starting from high temperatures at which equilibration is very rapid, the samples were cooled stepwise to the target temperature, equilibrated under constant-temperature conditions for an appropriate period, and then run at constant energy to collect data for subsequent comparisons. The statistical averages are taken from a period long enough for the average particle to diffuse at least 2.0 particle diameters as this is the surest way of ensuring ergodicity, for the reasons given below. The cooling
was then continued stepwise, with results being recorded from constant-energy runs made after equilibration, until ergodicity could no longer be restored in an accept-
able time (maximum run length 200 ps, except for the BKS and the modified Matsui potentials, for which the lowest temperature runs were extended to 300 and 400 ps, respectively).

Breaking of ergodicity can be detected in different ways:

1. In general, the temperature of a nonergodic system will not hold steady under constant-energy conditions because of the continuing conversion of potential to kinetic energy (or vice versa if the system is reequilibrating after a temperature up-jump).

2. In the $P-T$ isochores used to establish the position in temperature of the density maximum, loss of ergodicity is indicated by pressures that, in the negative expansivity regime below the density maximum, do not rise as much as expected from the ergodic data (however, see the unexpected development highlighted in the next section). This corresponds to the different degrees of expansion of the volume below the density maximum found for different cooling rates by Vollmayr et al. [28].

3. In diffusivity plots with data acquired with our descending temperature protocol, loss of ergodicity is indicated by diffusivity values that fall above the trend established by equilibrated samples. As pointed out long ago [34] and emphasized again recently [15, 39], it is the relaxational processes of amorphous systems, rather than spectroscopic or structural features, that are the most sensitive to the thermodynamic state and hence to the ergodicity or otherwise of the system. This important point is further substantiated by the data presented in this chapter.

Broken ergodicity is always associated with mean-square particle displacements substantially smaller than the value mentioned above, $2.0 \, d$, where $d$ is the diame-
ter of the particle. The criterion of (root-mean-square) distance diffused $>2$ particle diameters is based on the observation that structural relaxation times are, in the Stokes–Einstein approximation as well as in experiment, approximately the times needed for the average particle to diffuse $\sim d/3$ [40]. Equilibration, which we take to mean the decay of a perturbation to 2% of its initial value, requires the elapse of some 5–10 relaxation times, depending on the exponentiality or otherwise of the relaxation pro-
cess [41]. For processes observed on the time scales available to MD, departures from exponentiality are usually quite small.

Before leaving this section we note that, for the four-coordinated SiO$_2$ of this study, a strong finite-size effect has been detected in the dynamic properties, such that small samples relax more slowly than larger samples, an effect that persists until sample sizes exceed 8000 particles[42]. (This interesting effect, which we believe is a manifestation of the harmonicity of strong liquid structures, is expected to affect equally all the models studied here, although this needs to be established.)
6.1.3 Results

We present first the static functions (thermodynamic and structural) and then pass to the dynamic properties.

6.1.3.1 Heat Capacity and Glass Transition

All models show well-defined glass transitions (as in, e.g., Ref. [10]) at which the constant-volume heat capacity departs from its classical harmonic oscillator value of 24.4 J/mol K and rises by over 50% to values between 36 and 41.2 J/mol K, depending on the model. In this respect, all models are apparently at variance with experiment because $C_p$ in the laboratory experiment, although also reaching classical excitation in the glassy state, shows very little change at $T_g$. The observed change, is only $\sim 10\%$ [43, 44] at 1200°C, where the relaxation time reaches 100 s. $C_v$, which is the quantity obtained in the present simulations, must show even less (as $C_v < C_p$), except at the density maximum where the expansivity $\alpha$ is zero and $C_v < C_p$. Of course the experimental values are known at only lower temperatures, and it is quite possible that, if the measurements could be made, the laboratory substance would develop an increasing specific heat at higher temperatures (as BeF$_2$, a silica analog, tends to do).

Of the models studied, the BKS potential shows the largest $\Delta C_v$ and the TRIM potential shows the smallest. Both Matsui and TRIM potentials show a rapid decrease in $C_v$ at higher temperatures. The $T_g$ value for the BKS potential, indicated by the change of slope in the enthalpy–temperature relation, agrees with the temperature at which the anomalous low-$T$ expansion freezes, according to the study of Vollmayr et al., namely 3650 K [see Fig. 6.1.1(b)].

6.1.3.2 Density Maximum and Possible Higher-Order Transition

Turning now to the matter of the density maximum, we note that this occurs in the study by Vollmayr et al. at $\sim 4500$ K [28]. This is confirmed in the present study by the presence of an extremum at this temperature in the isochore $P$ versus $T$ seen in Fig. 6.1.1. As discussed many times before, the extremum in $P$ versus $T$ corresponds to a zero in the ratio of expansivity to compressibility, $\alpha/\kappa_T$, which can occur only if $\alpha$ passes through zero at a density maximum (or minimum). According to Fig. 6.1.1, a density maximum occurs for each of the potentials studied, but in every case the temperature of the maximum occurs far above the temperature of maximum density observed in the laboratory substance, 1820 K [9]. Indeed the laboratory phenomenon occurs at such a high viscosity that it would not be observable in a computer simulation made with an exact potential.

For some of the lowest temperature points in Fig. 6.1.1 (temperatures indicated by filled symbols), the data did not satisfy the criterion for ergodicity and hence do not represent the equilibrium behavior. The breaks in the $P-T$ plots therefore generally represent the breaking of ergodicity (however, see below).
Figure 6.1.1 Pressure–temperature isochores at density 2.20 g/cm$^3$ for SiO$_2$ liquid and glass in the different pair-potential representations indicated in the inset. A minimum pressure (or maximum tension) in the isochores indicates the existence of a density maximum. Filled symbols indicate nonergodic (glassy) states. Part (b) shows the isobaric variation of density, in which the density maximum is seen directly, from Vollmayr et al., with the BKS potential [28]. Part (c) shows the pressure fluctuations during passage of 180 ps of a constant-energy run at average temperature 2766 K and indicates the difficulty of obtaining precise isochore data at temperatures below the density maximum.

The temperature at which the density maximum occurs, $T_{\rho_{\text{max}}}$, in the different models is highest in the case of the TRIM potential, in which it is found at $\sim$9000 K, and lowest in the cases of the Tsuneyuki and the modified Matsui potentials, in which it falls at $\sim$4000 K. In the much-studied BKS case, $T_{\rho_{\text{max}}}$ is somewhat higher, $\sim$4500 K, but the pressure at the density maximum is quite negative. If the density were lowered so that the maximum density would be reached at ambient pressure, then $T_{\rho_{\text{max}}}$ would presumably fall at a somewhat lower temperature (but then the density would not be the experimental value. Note that this problem may be resolved by truncating the short-range interaction [28]. The truncation evidently not only economizes computer time but also leads to improved agreement with experiment.

For the modified Matsui potential, which is the most diffusive case (see Subsection 6.1.3.4 below), something more interesting may have happened. The point at 2750 K that failed to increase in pressure as expected was obtained from a run in which the ergodicity requirement was satisfied. This case was subjected to extended calculations to ensure that the values obtained represented equilibrium states. The fact that this extended study failed to change the value of $P$ at the lowest $T$ suggests that some sort of thermodynamic transition that arrests the anomalous expansion may have occurred.
in this case. This would be consistent with the presence of a compressibility maximum at \( T < T_{p_{\text{max}}} = 6000 \, \text{K} \) for the TRIM potential, seen with very lengthy equilibrations [12]. The density at which this isothermal compressibility maximum occurs, happens to be the same, 2.2 g/cm\(^2\), as that of all the Fig. 6.1.1 isochores. In this light, the near coincidence of the density versus temperature plots for the two slowest cooling rates in the study by Vollmayr et al. [28] may be interpreted as evidence that the observed behavior is the equilibrium (cooling-rate-independent) behavior (see Fig. 6.1.1 inset). This plot then indicates the presence of a rather sharp expansivity extremum at 3500 K for the BKS potential. Our data for the modified Matsui potential would indicate a more rounded “transition” at \( \sim 2750 \, \text{K} \).

Thus the case for a transition in the liquid state of SiO\(_2\), which might explain some of the differences between experiment and simulation, is strengthened. Indeed, a thermodynamic argument, due to Sastry et al. [45], shows that below any density maximum must lie a compressibility maximum. A compressibility maximum, like a heat capacity maximum, is usually regarded as a criterion for a (higher order) transition, and in some cases it may become a true phase transition i.e., a thermodynamic singularity. Unfortunately, we cannot draw any strong conclusions about this interesting matter from the present study because of the increasing magnitude of fluctuations (expected from increasing compressibility), which must be averaged over as the temperatures fall increasingly below \( T_{p_{\text{max}}} \). The situation is worsened by the fact that the fluctuations, which are structural in origin, have the time scale of the structural relaxation that is lengthening rapidly in the domain of interest. The fluctuations, which have short-time vibrational and long-time structural components, are illustrated in Fig. 6.1.1(c) which makes clear the problem of obtaining precise data in this domain. Further discussion of this interesting phenomenon will be deferred to future articles.

### 6.1.3.3 Bond-Angle Distribution

As mentioned above, the presence of a density maximum in the liquid is thought to be linked to temperature-dependent variations in the intertetrahedral angle distribution. According to the study by Vollmayr et al. [28], this angle is increasing with decreasing temperature at the lower temperatures as it was found to be largest in the glasses formed during the slowest cooling. We have compared this angle at 300 K for the different potential models cooled stepwise at the same effective rate \( 2 \times 10^{14} \, \text{K/s} \).

Figure 6.1.2 shows that the overestimate of the most probable intertetrahedral angle, which is a weakness of the TRIM potential, is largely rectified in the cases of the BKS and modified Matsui potentials. Differences in the widths of the distributions are discernible but are not readily characterized within the present data noise.

### 6.1.3.4 Diffusivities

Finally, Figs. 6.1.3 and 6.1.4 show the behavior of the diffusivities. Figure 6.1.3 shows the individual mean-square displacement plots, from whose long time slope the diffusivities are obtained, using the case of the modified Matsui potential. With
Figure 6.1.2 The SiO₂ glass intertetrahedral angle distribution for the different pair potentials listed in the inset. The effective cooling rate, $2 \times 10^{14}$ K/s, was the same in each case. Experimental estimates (summarized in Ref. 15) range from 144° to 153°.

Figure 6.1.3 Mean-square displacement of oxygen species as a function of time for the modified Matsui potential. The inset shows the two lowest temperatures studied. The displacement at 2482 K is insufficient to give a valid measure of the ergodic diffusivity. The displacement at 2766 K is marginally sufficient.
one exception, data points are not included in Fig. 6.1.4 unless the mean-square displacement during the constant-energy run is greater than 2.0 oxide-ion diameters. The exception is the lowest temperature point (2482 K) of Fig. 6.1.3 for the modified Matsui potential for reasons that are given below.

Figure 6.1.4 then shows the collection of diffusivity Arrhenius plots for the different potentials and includes experimental data based on use of the Eyring equation [46] to convert the viscosity data measured in the temperature range 1500–2800 K to oxygen diffusivities. The most recent justification for this conversion formula is found in the work of Poe et al. [17]. The jump distance used is the same as that in Refs. [10], [17], and [46], viz., the oxide-ion diameter, 0.28 nm. At the temperatures of simulation the diffusivities of Si and O are very similar, so the Si values are omitted in most cases.

At temperatures near the experimental $T_g$ it seems that the oxide-ion diffusivity is much the larger, i.e., a decoupling of the two occurs [47] as is also seen in high-pressure simulations [3]. It should also be remembered, in comparing these diffusivities with experiment, that dynamic properties of small SiO$_2$ systems at normal densities are subject to finite-size effects that slow down the response functions relative to those of large systems, $>$8000 ions [42]. The effect amounts to some 500% in D for 450-ion systems and can be expected to be similar for all the potentials of this study as it is a function of the same harmonicity that allows the other liquid-state anomalies to
show up above thermal smearing effects. Because the effect can be linked to the more harmonic behavior of the strong liquids, it is likely to be more pronounced at the lower temperatures. This might account for the very low values of $D$ obtained for the modified Matsui potential at the lowest temperature at which, because of (Fig. 6.1.3, inset), an overestimate would have been expected.

In Fig. 6.1.4 we see, at the lowest common temperature, 6000 K, a spread of oxygen diffusivities for the different pair potentials that approaches 2 orders of magnitude. The modified Matsui potential gives quite the highest diffusivity, whereas TRIM and Kubicki potentials group together as the least diffusive. There are two slightly different versions of the TRIM potential result. That marked Poole et al. was obtained with the original Woodcock–Angell–Cheeseman potentials (see Ref. [1], Table 2, and appended notes), and the other was obtained with the parameters listed in Ref. [4].

### 6.1.4 Discussion

The comparison of results given in Figs. 6.1.1–6.1.4 is quite instructive. It shows that although the modified Matsui potential gave the best representation of the IR spectrum, and also yields the temperature of maximum density closest to the experimental value, it yields a diffusivity behavior that is quite incompatible with the experimental behavior. The simulated temperature range extends to 2750 K. This overlaps the experimental viscosity range, which extends to 2800 K. We find a discrepancy of some 4 orders of magnitude at 2800 K, and it will be increased even further by the finite-size effect. Thus we find that, although the time scale for oscillation of the particles in their potential minima is relatively well represented by the modified Matsui potential, the probability of their escaping from the potential minimum and thus diffusing is grossly overestimated. This implies that although the shape of the potential near its minimum is quite accurate, the curvature at distances more removed from the minimum is not well represented. In the latter respect the original TRIM potential, the Kubicki potential, and the BKS potential are all superior.

The TRIM potential diffusivity data, which show a moderate curvature, appear to be on a natural course to connect to the experimental data. The BKS data, although at first sight appearing to be too diffusive to be compatible with the Arrhenius experimental data, show considerable curvature, and if this accelerates, as observed for TRIM SiO$_2$ at higher densities [49], the data could conceivably join up with the experiments.

Recent extensions of the Ref. [28] studies, by Horbach et al. [50], in which extremely long runs were used, however, show a return to Arrhenius behavior at the lowest temperatures, presumably after passage through a thermodynamic transition of the sort we have discussed above. Such behavior would imply the existence of an interesting crossover in the liquid state from fragile to strong behavior as a function of temperature alone, as seems to be the case for H$_2$O according to simulation studies by Tanaka [51] and Sciortino et al. [29] and according to evidence from experimental data from Angell and co-workers [52, 53]. The apparent equilibrium cessation of the anomalous
expansion observed in Fig. 6.1.1 for the modified Matsui potential would presumably be thermodynamic evidence that such a transition can occur. Previously, evidence for a (continuous) strong liquid to fragile liquid transition in SiO$_2$ has been provided only by behavior under compression [54, 55].

The possibility that a higher-order transition occurs within the liquid state of SiO$_2$ is a matter of great interest as the existence of such a transition would link the behavior of silica into the phenomenology of H$_2$O even more strongly than has been suggested to date [12, 49]. In laboratory SiO$_2$, however, it would seem to be possible only as a sub-$T_g$ phenomenon, as the density maximum, below which the transition would have to occur, lies at 1800 K. Furthermore, confusion arises from the fact that laboratory SiO$_2$ is already a strong liquid at higher temperatures. This problem is certainly one that deserves further study [56]. We point out that the imminence of a compressibility maximum near $T_g$ is susceptible to a convenient laboratory study with ambient-temperature x-ray-scattering determinations of density fluctuations that are frozen on quenching samples that have been equilibrated at different temperatures near and below the normal (10 K/min) glass transition.

As far as the best of the currently available pair potentials for SiO$_2$ simulations is concerned, the BKS potential seems to give a good representation of all aspects of the laboratory material’s behavior [28, 50, 55], although it evidently needs further adjustment to yield a lower temperature for the maximum density (which will necessarily be pushed below the ergodicity curtain in the case of an accurate potential) and a wider splitting of the IR spectrum.

6.1.5 Conclusions

Our results highlight problems with, as well as strengths of, the pair potentials that have been proposed for the simulation of liquid SiO$_2$. It has been shown that pair potentials that will reproduce the behavior of silicalike systems are not only of importance to geophysics but are also of interest in the overall development of liquid-state phenomenology. The existence of waterlike anomalies and the associated possible existence of second critical points [30, 31] and even first-order polyamorphic transitions [57] in these quasi-ionic systems suggest that the further investigation of such potentials will be rewarding. Concerning the simulation of laboratory SiO$_2$, however, it must be concluded on the basis of the present study and the earlier vibrational spectroscopy simulations that a really adequate pairwise additive model has not yet been developed.

Acknowledgment

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References


[2] This question was also examined, with the same results, for the analog weakened network system BeF$_2$ [B. Boulard, C. A. Angell, J. Kieffer, and C. C. Phifer, J. Non-Cryst. Solids 140, 350 (1992)].


[38] The problem of high-temperature instability arises in the BKS and Tsuneyuki potentials from the way repulsion vanishes at small r values because of the parameters in the short-range van der Waals attractive terms. Such small r values are not seen in the range of temperatures originally studied with these potentials, but are obtained in higher-temperature studies, with disastrous consequences. To avoid the problem we follow Vollmayr et al. [28] in replacing the original potential function with a harmonic potential when $r_{ij}$ is smaller than a critical distance [for BKS $r_{c(Si-O)} = 1.1936 \text{ Å}$, $r_{c(O-O)} = 1.439 \text{ Å}$, and for Tsuneyuki, $r_{c(Si-O)} = 1.280 \text{ Å}$, $r_{c(O-O)} = 1.510 \text{ Å}$].


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