Finite-size effects in silica: a landscape perspective

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Abstract
Finite-size effects are analysed for the well-known BKS model of silica. Results are presented for thermodynamic as well as dynamic observables which play a key role in the analysis of the potential energy landscape. It turns out that, for the analysed temperature range ($T \geqslant 3000$ K), a system with only $N = 99$ particles does not display significant finite-size effects in thermodynamic observables. In agreement with previous work, one observes finite-size effects for the dynamics. However, after rescaling of time the finite-size effects nearly disappear. These results suggest that for BKS-silica a system with only $N = 99$ particles is sufficiently large to study important properties of structural relaxation in the temperature range considered.

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

1. Introduction

For a better understanding of the underlying nature of the glass transition it has been proven fruitful to use the concept of the potential energy landscape (PEL) (Goldstein 1969, Stillinger and Weber 1982, Debenedetti and Stillinger 2001). In this framework the low-temperature dynamics can be interpreted as hops between minima of the potential energy, denoted inherent structures (IS). Going a step further one may even join adjacent IS, thereby forming metabasins (MB) (Buechner and Heuer 2000, Doliwa and Heuer 2003a, 2003b, Denny *et al* 2003). Qualitatively, one has achieved a discretization of the dynamics. Each MB is characterized by its energy and its waiting time, i.e. the time the system needs to leave an MB. It has been shown that to a very good approximation the temperature dependence of the diffusion constant can be quantitatively related to the inverse of the average MB waiting time. Thus, the macroscopic transport can be explicitly expressed in terms of locally defined MB waiting times. Furthermore, a strong relation exists between the energy and the waiting time, thus establishing a strong tie between thermodynamic and dynamic aspects of supercooled liquids.

Relaxation processes in supercooled liquids are spatially localized (Wales 2003). When studying a very large system one would thus observe many independent relaxation processes. As a consequence the total energy, and in particular its temporal evolution, is a sum of many more or less independent contributions. This gives rise to major averaging effects. Thus, in

recent years it has become popular to study relatively small systems (using periodic boundary conditions, of course) to avoid this effect as much as possible; see, e.g., Denny *et al* (2003), Doliwa and Heuer (2003a), Appignanesi *et al* (2006). Naturally, for too small systems finite-size effects start to dominate the properties of the system. Therefore, the ideal system size is determined by the condition that it is the smallest system for which finite-size effects are not relevant.

For every system this has to be studied individually. In our previous work on the binary Lennard-Jones mixture we have shown that $N = 65$ is sufficient for the range of temperatures accessible to computer simulations (Doliwa and Heuer 2003c). An important aspect of the analysis was the comparison of a system with $N = 65$ and with $N = 130$ particles. More specifically, we have checked the hypothesis (H_{65}) that a system with $N = 130 = 2 \times 65$ particles behaves exactly as if it were a superposition of two strictly independent systems with $N = 65$ particles. (H_{65}) turned out to be true first for the distribution of MB, reflecting the thermodynamics, and, second, for the dynamics. There we have predicted the distribution of waiting times for $N = 130$ under (H_{65}) and have checked that the result agrees very well with the actual waiting time distribution.

Here we study the case of BKS-silica (van Beest *et al* 1990) which has been of major interest due to its special role as a very strong glass-former (Horbach *et al* 1996, Horbach and Kob 1999, Saika-Voivod *et al* 2001, Shell *et al* 2002, Saika-Voivod *et al* 2004). We will justify that our previous choice of $N = 99$ particles (Saksaengwijit *et al* 2004, Saksaengwijit and Heuer 2006a, 2006b) is very reasonable. Actually, the finite-size discussion for BKS-silica is somewhat more complicated because it is known that, for example, the diffusion constant and the α-relaxation time τ_α have a strong dependence on the system size (Horbach *et al* 1996). Despite these differences the incoherent scattering function $S(q, t)$ can be scaled on each other for different $N \geqslant 60$ (Saksaengwijit *et al* 2004). Thus, one may speculate that after rescaling of time the underlying nature of the dynamics is unchanged when comparing very small systems with macroscopic systems. Actually, some pieces of evidence for this interpretation have been already reported (analysis of configurational entropy (Saksaengwijit *et al* 2004), properties of tunnelling systems (Reinisch and Heuer 2005), activation energy of oxygen diffusion (Saksaengwijit *et al* 2004)).

In this paper we analyse the nature of the finite-size effects more systematically by checking (H_{99}) when comparing $N = 99$ and $N = 198 = 2\times99$. The choice of thermodynamic and dynamic observables is governed by our ultimate goal of understanding the glass transition in terms of PEL properties. Additional results for smaller and larger systems are included to convey a general picture of the finite-size effects. Technical information about the BKS-silica simulations can be found in Saksaengwijit *et al* (2004) and Saksaengwijit and Heuer (2006a). We mainly present data for $T = 3000$ K.

2. Thermodynamics

A central observable is the Boltzmann energy distribution $p(e, T)$ of MB visited by the system at a fixed temperature T. It is shown for different system sizes in figure 1. Whereas the range of energies is somewhat comparable for all system sizes, one can clearly see that for $N \leqslant 30$ there exist some specific energies with high population. Closer analysis reveals that during the temporal evolution the system always comes back to the same configuration except for permutation of particles. Their presence dominates the thermodynamics as well as the dynamics. Similar effects have been already seen in Lennard-Jones systems (Heuer 1997, Buechner and Heuer 1999, Keyes and Chowdhary 2002). In contrast, for $N \geqslant 60$ one has a continuum of configurations.
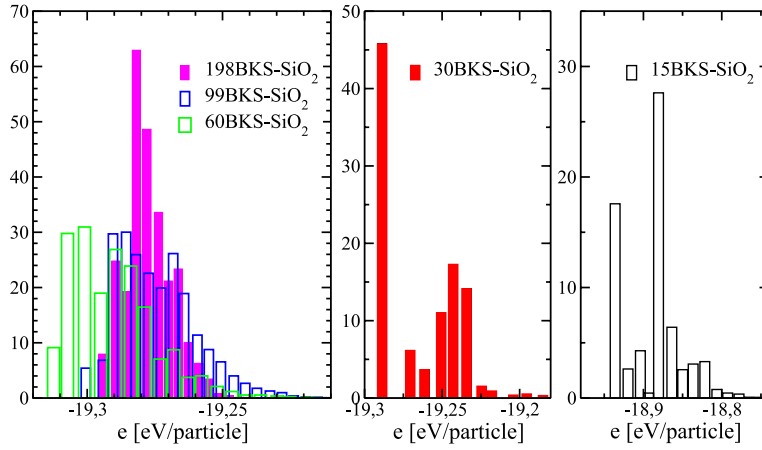
Figure 1. The histograms of $p(e, T)$ for different system sizes at $T = 3000$ K.
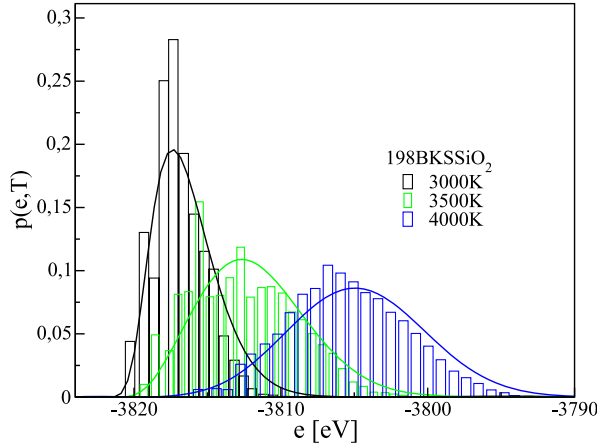

Figure 2. The histograms of $p(e, T)$ for $N = 198$ at various temperatures. Via $G_{198,\text{eff}}(e)$, predicted from equation (1), we estimate $p(e, T) \propto G_{198,\text{eff}}(e) \exp(-\beta e)$. They are shown as solid lines.

Now we may check whether (H$_{99}$) is fulfilled. If the anharmonic contributions are small (which is the case for $T \leqslant 4000$ K) one can write $p(e, T) \propto G_{\text{eff}}(e) \exp(-\beta e)$, where $G_{\text{eff}}(e)$ is the full energy distribution of MB (including a possible dependence of harmonic force constants on energy) (Sciortino *et al* 1999, Buechner and Heuer 1999). With (H$_{99}$) one obtains

$$G_{198,\text{eff}}(e) = \int de' \, G_{99,\text{eff}}(e') G_{99,\text{eff}}(e - e'). \tag{1}$$

This can be translated into a prediction for $p(e, T)$ for $N = 198$ based on the properties of $N = 99$. The results are shown in figure 2.

One can clearly see that the agreement is close to perfect apart from a minor constant downward shift of energy for $N = 198$ which, however, is irrelevant for the thermodynamic properties. Note that the very good agreement implies that the cutoff in the PEL, reported for $N = 99$ (Saksaengwijit *et al* 2004), is also there for $N = 198$, albeit more smeared out for trivial statistical reasons. Actually, a similar analysis shows that, starting from $N \geqslant 60$ atoms, thermodynamic finite-size effects become small.
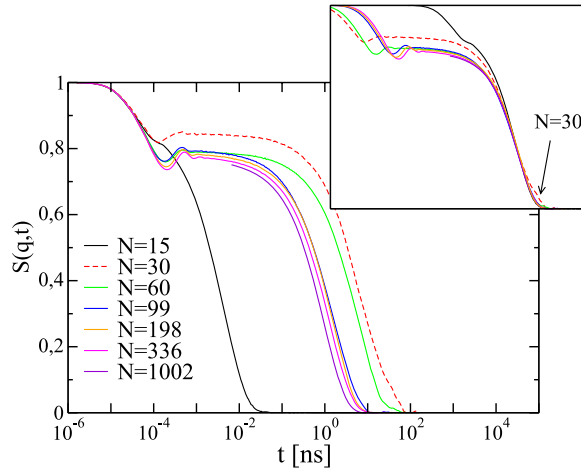
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Figure 3. Incoherent intermediate scattering function $S(q,t)$ with a wavevector $q = 1.7$ Å^{-1} for different system sizes at 3000 K. The inset shows $S(q,t)$ after scaling the time axes, respectively.

3. Dynamics

A central observable for the dynamics is the incoherent scattering function $S(q,t)$ analysed close to the wavevector of the maximum of the structure factor. The results for $T = 3000$ K are shown in figure 3. One can clearly see that, apart from the artificially small system of $N = 15$ particles, $S(q,t)$ displays the typical two-step decay, characteristic for supercooled systems. Strictly speaking, up to the largest system size of $N = 1002$ one observes finite-size effects, and even up to $N = 3006$ the curves will further shift, i.e. the plateau value as well as the α-relaxation time τ_α decreases. However, for $N \geqslant 99$ this shift is relatively small (a factor of 1.8 for τ_α when comparing $N = 99$ and 1002). Actually, for the diffusion constant it has been numerically shown for a similar temperature that the timescale shifts by a factor of approximately $\exp(-80/N)$, which for the present case would predict a factor of 2.1, in agreement with the above value (Zhang *et al* 2004).

Strictly speaking, one cannot define (such as in the case of Lennard-Jones systems (Doliwa and Heuer 2003c)) a system size $N^\star$ such that the finite-size effects are significant for somewhat smaller system sizes, and basically disappear for $N > N^\star$. Fortunately, this change in behaviour around some system size is recovered if one allows for scaling of the time axis; see the inset of figure 3. It turns out that for $N \geqslant 60$ the different curves are very similar. To quantify this effect we have fitted the α-relaxation part of $S(q,t)$ with a stretched exponential $\exp(-(t/\tau)^\beta)$. One obtains a dramatic shift of β when going from $N = 30$ ($\beta = 0.65$) to $N = 60$ ($\beta = 0.80$). Upon further increase of N one observes a systematic but small increase of β to 0.86 for $N = 1002$. This is a first hint that apart from a scaling factor the α-relaxation dynamics of silica, as expressed by $S(q,t)$, only shows very small finite-size effects.

This conclusion can be corroborated from analysis of the whole MB waiting time distribution, which is a very sensitive measure for the nature of relaxation processes in glass-forming systems (Doliwa and Heuer 2003a, Denny *et al* 2003). Using (H$_{99}$) it is possible to predict the MB waiting time distribution $p(\log \tau)$ for $N = 198$ particles based on the distribution for $N = 99$; see Doliwa and Heuer (2003c) for more technical details. The result is shown in figure 4. After scaling the time axis of the predicted distribution for $N = 198$ by a factor of approximately 1.3, one obtains a surprisingly good agreement between the prediction and the actual waiting time distribution for $N = 198$. This strongly supports the interpretation
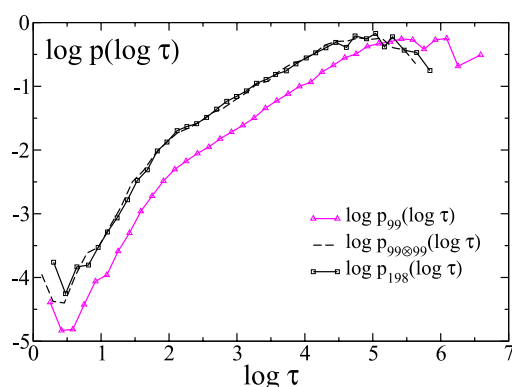
Figure 4. Distribution of MB waiting times for $N = 99$ and $N = 198$ at $T = 3000$ K. Further included is the estimation for $N = 198$ based on the central hypothesis (H_{99}). The time axis for this curve has been shifted by a factor of 1.3.

that apart from a scaling factor finite-size effects are not relevant for $N = 99$. Actually, this scaling factor is (if at all) only weakly temperature dependent. This is the reason why the low-temperature activation energy for $N = 99$ is nearly identical to that of $N = 1002$ (Saksaengwijit *et al* 2004).

The comparison in figure 4 also reveals that long waiting times are missing for $N = 198$ (as expected from our theoretical predictions). These long-lived MB represent the extremes of the heterogeneities of the landscape. The apparent disappearance of the long-time tail for $N = 198$ again shows that interesting information is averaged out for simple statistical reasons when increasing the system size.

4. Summary

We have revisited the question of finite-size effects in silica. From previous work it was clear that significant finite-size effects (a factor of 2 in the diffusion constant) are present when going to system sizes significantly smaller than 1000 particles. However, the present work has revealed that for many types of analysis a system size of $N = 99$ is already sufficient in the range of temperatures accessible to present-day computer simulations. In particular we have shown that the thermodynamic properties, relevant for the landscape analysis, do not show any relevant finite-size effects. For the dynamic properties, related to the coarse-grained description of the MB and thus to the late β- and the α-relaxation regime, the finite-size effects for $N = 99$ for $S(q, t)$ and the waiting time distribution become very small after a simple scaling of the time axis. Thus, with respect to finite-size effects BKS-silica behaves very similarly to the Lennard-Jones system except for some additional (nearly temperature-independent) scaling of the time axis.

Naturally, the large length scales, obtained from analysis of higher-order correlation functions (see, e.g., Glotzer *et al* (2000)), would very likely show much stronger finite-size effects. The interesting question emerges why this is not reflected in the two-time correlation function $S(q, t)$.

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