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Multiple reentrant glass transitions of soft spheres at high densities: Monotonicity of the curves of constant relaxation time in jamming phase diagrams depending on temperature over pressure and pressure

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By using molecular-dynamics simulations, we determine the jamming phase diagrams at high densities for a bidisperse mixture of soft spheres that interact according to repulsive power-law pair potentials. We observe that the relaxation time varies nonmonotonically as a function of density at constant temperature. Therefore, the jamming phase diagrams contain multiple reentrant glass transitions if temperature and density are used as control parameters. However, if we consider a new formulation of the jamming phase diagrams where temperature over pressure and pressure are employed as control parameters, no nonmonotonic behavior is observed.

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I. INTRODUCTION

The dynamics of soft particles usually slows down when either the temperature is decreased or the packing fraction is increased. A glass former consisting of soft spheres that interact according to repulsive power-law interaction potentials when they overlap is a commonly used model system in order to study jamming or glassy dynamics (for reviews see, e.g., [1–3]). A particular problem of great interest is the relation of the glassy dynamics of such soft spheres and hard spheres (see, e.g., [4–10]). While local rearrangements of soft spheres occur if particles cross finite-energy barriers, rearrangements of hard spheres depend on the free volume or a global cooperative reorganization. Furthermore, hard spheres were characterized as a fragile glass former as a function of packing fraction, whereas soft spheres might also lead to strong glassy dynamics [4,5,11].

In the case of small overlaps corresponding to systems with small densities or at low pressures the dynamics of soft spheres is similar to the one of hard spheres [7–9]. At high densities or for large overlaps a different behavior was reported [12–15]. For example, if the density of a system with only moderate overlaps is increased the dynamics first slows down and a glass transition might occur at sufficiently low temperatures. However, if the density is increased further a reentrant melting transition was observed where the dynamics becomes faster for increasing density or pressure [13–15]. Note that we use the term glass transition in the sense that the relaxation time exceeds the time accessible in the simulations.

At very high densities, if more than two particles overlap and spheres start to interact with their next to nearest neighbors, another glass transition with subsequent reentrant melting can be observed. Moreover, as reported in [15], a whole series of such successive glass and reentrant melting transitions might occur. The corresponding nonmonotonous behavior of the diffusion coefficient as a function of density is shown in [15] for a two-dimensional system. In this article we present results of similar simulations in a three-dimensional system. Furthermore, we determine the complete jamming phase diagrams for different exponents of the interaction potential.

Jamming phase diagrams are employed to plot the dependence of the dynamics on different control parameters in a well arranged way [16]. Originally, the inverse density or inverse packing fraction, the temperature, and the applied stress were used as control parameters [1,16]. In a jamming phase diagram the jamming surface or surfaces of constant relaxation time are shown as a function of the control parameters. As we will show in the following, due to the reentrant glass transitions the jamming surface for soft spheres is not monotonous.

Recently, a new formulation of the jamming phase diagram was proposed [8]. It uses a different set of control parameters, namely temperature over pressure, pressure, and shear stress over pressure. As shown in [8] an advantage of the new jamming phase diagram is that the hard-sphere behavior is given by the plane where the pressure vanishes and is therefore easily accessible in the diagram. Furthermore, point J, i.e., the point where after an instantaneous quench from infinite to zero temperature the system cannot avoid overlaps without crossing energy barriers [17,18], is located in the origin which offers new insights to paths approaching point J [8]. Note that recent works indicate that athermal jamming and the glass transition are distinct phenomena [19–21]. Here we present another advantage of the new set of control parameters. As we will show, despite the reentrant glass transitions, within the jamming phase diagrams spanned by the new control parameters, all curves of constant relaxation time are monotonous for all parameters that we have checked.

There are particles, e.g., star-shaped polymers [11,22,23], that interact according to soft interaction potentials and for which large overlaps are possible. Therefore, we expect that the reentrant glass transitions also occur in such systems and should in principle be accessible to experiments.

The article is structured as follows. In Sec. II we introduce the model system. The relaxation time as a function of density for constant temperature is presented in Sec. III. Jamming phase diagrams with density and temperature as control parameters are shown in Sec. IV. In order to compare different control parameters, we discuss pressure as a function of density in Sec. V before the jamming phase diagrams with temperature over pressure and pressure as control parameters are presented in Sec. VI. Finally, we conclude in Sec. VII.

II. SYSTEM

We consider a bidisperse mixture of soft spheres in three dimensions. Half of the spheres have the diameter σ, the other half are larger spheres with diameter 1.4σ. All particles have mass m. The spheres interact according to a repulsive power-law potential,

$$V(r_{ij}) = \begin{cases} \frac{\epsilon}{\alpha}\left(1 - \frac{r_{ij}}{\sigma_{ij}}\right)^{\alpha} & \text{for} \quad r_{ij} < \sigma_{ij}, \\ 0 & \text{for} \quad r_{ij} \geqslant \sigma_{ij}, \end{cases} \tag{1}$$

where r_{ij} is the distance between two spheres and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ is their average diameter. We consider the exponents $\alpha = 3/2$, $\alpha = 2$ leading to a harmonic potential, $\alpha = 5/2$ for Hertzian interactions, and $\alpha = 3$.

We perform molecular-dynamics simulations with $N = 1000$ spheres at fixed temperature T and pressure p for a system with periodic boundary conditions using the constraint method by Evans and Morris [24]. We extract the number density ρ and determine the relaxation time τ that we define as the time where the mean square displacement is $\langle r^2(\tau)\rangle = \sigma^2$. Each value of τ and ρ presented in the following is averaged over the results of three independent runs.

III. ISOTHERMAL PATHS

First, we determine the relaxation time τ as a function of density ρ along isothermal paths (see Fig. 1). Starting at low densities the relaxation time first increases for increasing density. This is the normal behavior one expects for the colloidal dynamics close to the glass transition. For sufficiently small temperature τ exceeds the time that is accessible in our simulations. However, when ρ is increased even further, the relaxation time suddenly decreases. As already discussed in [13–15] the decrease of τ with increasing ρ is due to completely overlapping particles. Unlike hard spheres, soft spheres can also rearrange by crossing neighboring spheres. At height densities soft spheres even overlap in the athermal limit [15]. Therefore, the effective potential barrier that a sphere has to cross for a rearrangement is smaller and as a consequence the relaxation time decreases.

For small α, e.g., $\alpha = 1.5$ or $\alpha = 2$ as depicted in Figs. 1(a) and 1(b), respectively, the relaxation time possesses more than one maximum. Therefore, multiple glass transitions with subsequent reentrant melting transitions occur. While the first reentrant melting is due to three spheres starting to overlap, the following reentrant transitions are caused by a forth, fifth, etc. sphere beginning to imbricate.

For softer spheres, i.e., a larger exponent α, we only observe one glass transition with subsequent reentrant melting. For soft interactions four or more particles start to interact already at a lower density, even due to thermal excitations. Therefore, there is no sharp density where an additional sphere begins to interleave its neighbors. In Sec. V we discuss how density and pressure are connected, which also is an indicator on how many spheres are overlapping and how sharp the crossovers for additional overlaps are.

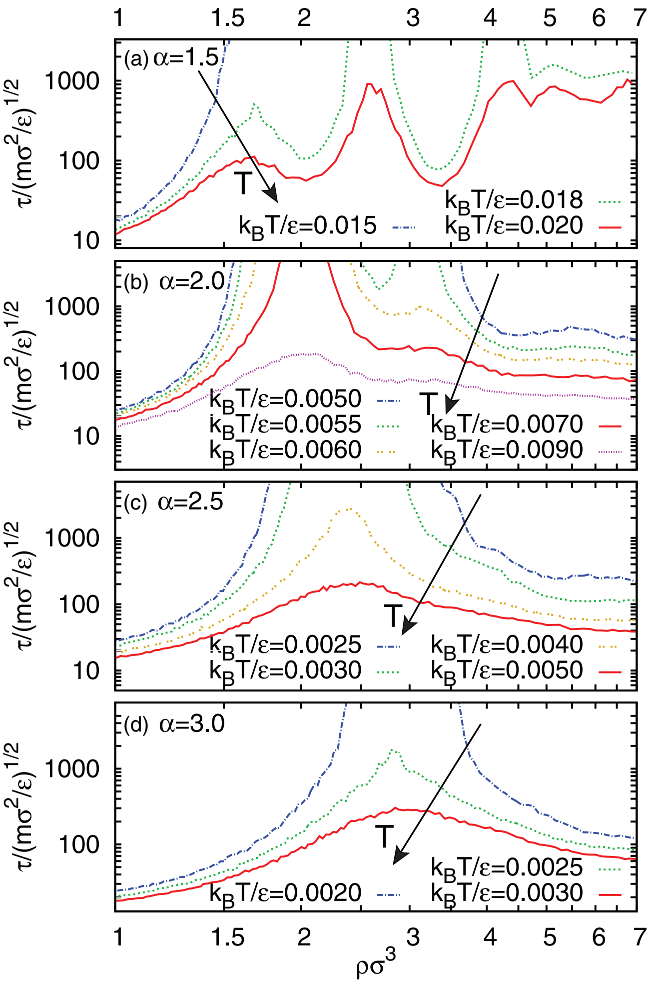

FIG. 1. (Color online) Relaxation time τ as a function of density ρ for selected constant temperatures T. The exponent of the interaction potential is (a) $\alpha = 1.5$, (b) $\alpha = 2$, (c) $\alpha = 2.5$, and (d) $\alpha = 3$. The relaxation time is given in units of $(m\sigma^2/\epsilon)^{1/2}$.

IV. JAMMING PHASE DIAGRAMS DEPENDING ON TEMPERATURE AND DENSITY

In Fig. 2 we show the jamming phase diagrams. The axes denote the temperature T and the number density ρ. Both axes are plotted logarithmically. The curves mark parameters with constant relaxation time τ. Below the solid black line that denotes the relaxation time $\tau = 1000\sqrt{m\sigma^2/\epsilon}$ the relaxation time exceeds the time scale of our simulations and within that time scale the system is jammed. Note that the relaxation times that are depicted by the lines increase exponentially when crossing the curves from top to bottom. Therefore, the diagrams clearly show the non-Arrhenius increase of τ for decreasing T. Furthermore, the oscillating behavior of the curves, especially for $\alpha = 1.5$ or $\alpha = 2$ as shown in Figs. 2(a) and 2(b), exposes the multiple reentrant glass and melting transitions.

In Fig. 3(a) we directly compare the lines that denote the relaxation time $\tau = 1000\sqrt{m\sigma^2/\epsilon}$ for different exponents α. As already mentioned in the previous section, multiple reentrant transitions can be observed for small α, while for softer spheres with larger α the multiple reentrant behavior is

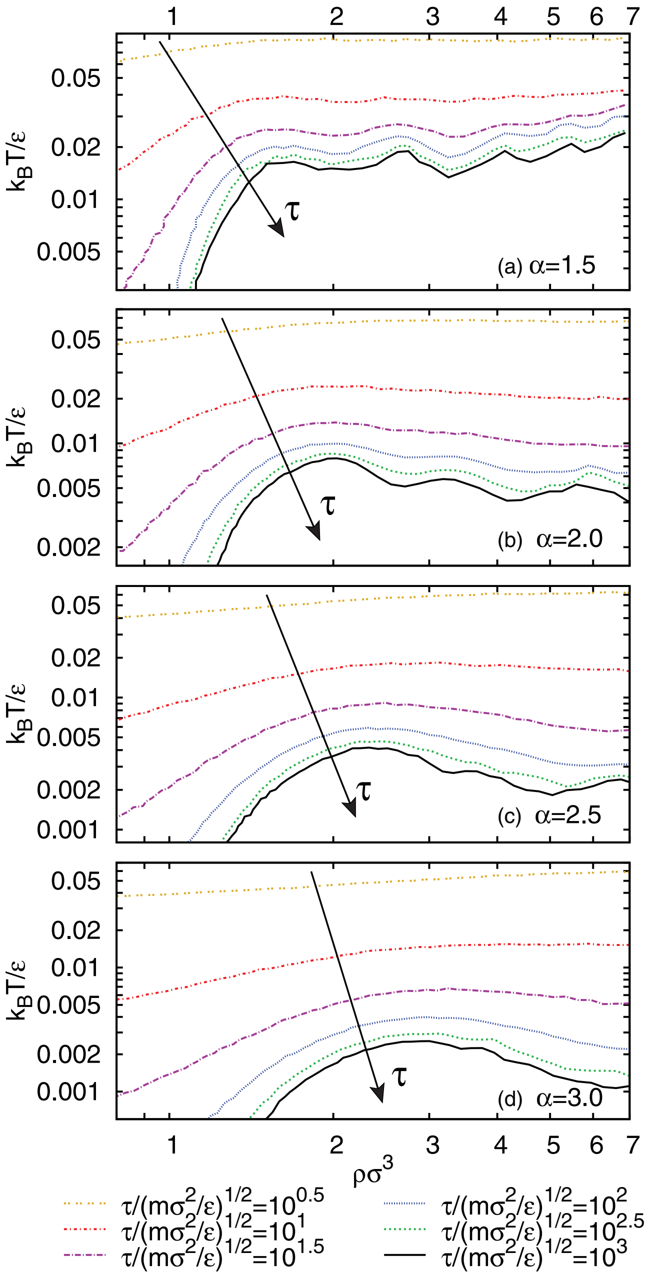

FIG. 2. (Color online) Jamming phase diagrams depending on temperature T and number density ρ. Each curve denotes states where the same relaxation time is observed. Therefore, below the solid black line that corresponds to relaxation times $\tau/(m\sigma^2/\epsilon)^{1/2} = 10^3$ the time scale of rearrangements exceeds the maximal time of our simulations. Time is given in units of $(m\sigma^2/\epsilon)^{1/2}$. The exponent of the interaction potential is (a) $\alpha = 1.5$, (b) $\alpha = 2$, (c) $\alpha = 2.5$, and (d) $\alpha = 3$.

less pronounced. Finally, for $\alpha = 3$ only one maximum occurs, i.e., there is only one glass transition with subsequent reentrant melting.

Since in some articles time is given in units of $\sqrt{m/(p\sigma)}$ instead of $\sqrt{m\sigma^2/\epsilon}$ (see, e.g., [7–9,25]), we show lines of constant relaxation time in units of $\sqrt{m/(p\sigma)}$ in Fig. 3(b). We do not observe any qualitative differences between the two representations of the jamming phase diagrams in Figs. 3(a) and 3(b) that only differ by the unit of time. Therefore, the multiple reentrant glass are not an artifact of the employed time unit. However, as we will show later, by changing the control parameters, jamming phase diagrams can be constructed such that the lines of constant relaxation time are monotonous.

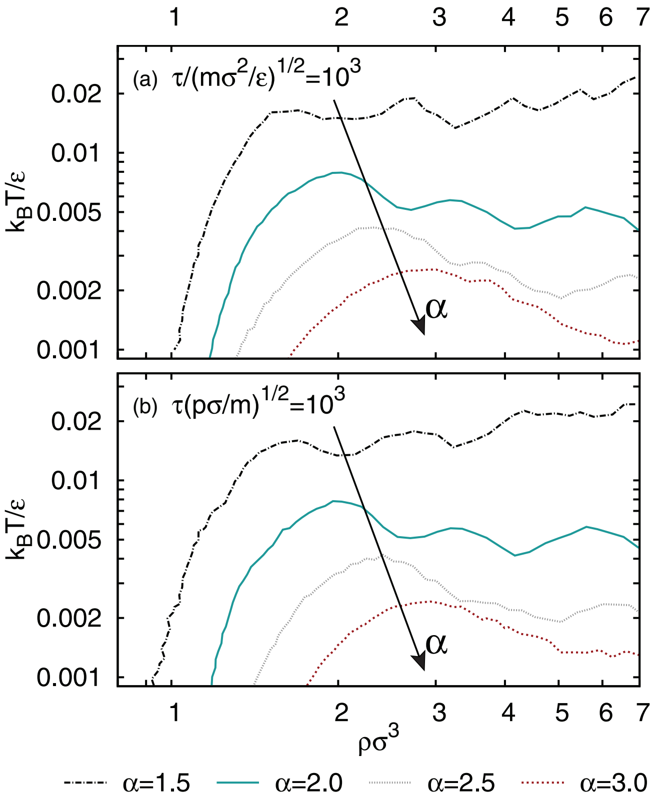

FIG. 3. (Color online) Comparison of lines with constant relaxation time (a) $\tau = 1000\sqrt{m\sigma^2/\epsilon}$ and (b) $\tau = 1000\sqrt{m/(p\sigma)}$ for different exponents α. Temperature T and number density ρ are used as control parameters. Note that (a) and (b) differ by the employed unit of time.

V. PRESSURE AS A FUNCTION OF DENSITY

As already mentioned in Sec. III the nonmonotonous behavior of the relaxation time as a function of density is due to the possibility of overlaps of multiple spheres. If the density is increased the dynamics slows down every time new pairs of particles start to interact, e.g., at low densities all spheres start to overlap with their nearest neighbor, for further increased density after the first reentrant transition the dynamics slows down again due to interactions with the next to nearest neighbors, etc. On the other hand, the reentrant melting is observed whenever the particles overlap significantly but no additional contacts or overlaps occur if the density is slightly increased. For the athermal limit and for two-dimensional systems this behavior is also studied in [15].

The sequence of an increase of the number of new contacts followed by increasing overlaps but no new interacting pairs of particles also leads to a nontrivial dependence of the pressure on density. In Fig. 4(a) we show the pressure as a function of number density. The derivative of the pressure with respect to the density is plotted in Fig. 4(b). The solid red curves in Fig. 1 represent a typical case where multiple reentrant

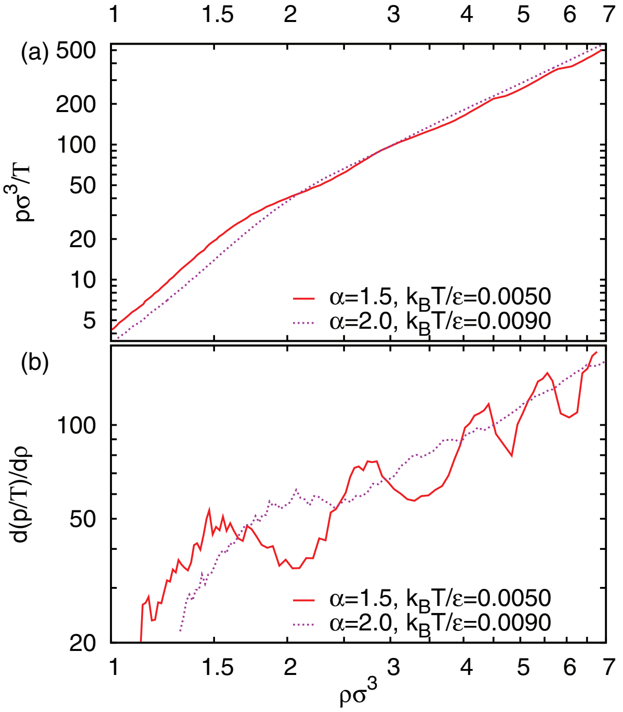

FIG. 4. (Color online) (a) Pressure as function of the number density for a case where multiple reentrant glass transitions are observed ($\alpha = 1.5$, $k_BT = 0.05\epsilon$, solid red line) and a case where only one glass transition with subsequent reentrant melting occurs ($\alpha = 2.0$, $k_BT = 0.09\epsilon$, dotted magenta line). (b) Derivatives of the curves in (a) that demonstrate the nontrivial dependence of the pressure on density.

glass transitions are observed, while the dotted magenta curves denote a case where only one maximum of the relaxation time exists. Accordingly, in Fig. 4(b) the solid red curve shows an oscillating behavior, while the dotted magenta curve only possesses one local maximum. The pressure dependence can be explained by overlaps between the spheres. If new pairs of spheres start to interact the pressure increases rapidly. This corresponds to the density ranges where the dynamics becomes slower. However, whenever an increase of the density only causes increasing overlaps but no new contacts, the increase of pressure is smaller. This coincides with the densities where the relaxation times are small.

VI. JAMMING PHASE DIAGRAMS DEPENDING ON TEMPERATURE OVER PRESSURE AND PRESSURE

In a new formulation of the jamming phase diagram [8] temperature over pressure T/p and pressure p are used as control parameter. The different control parameters are motivated by a number of advantages of the new formulation. For example, temperature over pressure is a suitable control parameter to characterize both the glass transition at low temperatures and the colloidal glass transition at large densities [7,25]. Therefore, in a jamming phase diagram with the new control parameters a universal limit corresponding to the hard sphere case is approached for $p \to 0$ [8].

In Fig. 5 we plot the lines of constant relaxation time as function of the control parameters temperature over pressure T/p and pressure p. Interestingly, for all cases we have studied all curves are monotonous. There is a steplike behavior for low temperatures that is the remainder of the nonmonotonous behavior in the old formulations of the jamming phase diagrams. Within the new diagrams, no reentrant transitions occur for all horizontal or vertical paths. The isothermal paths presented in Sec. III correspond to paths along hyperbolic curves in the new diagrams (straight lines with slope −1 in the log-log plots of Fig. 5).

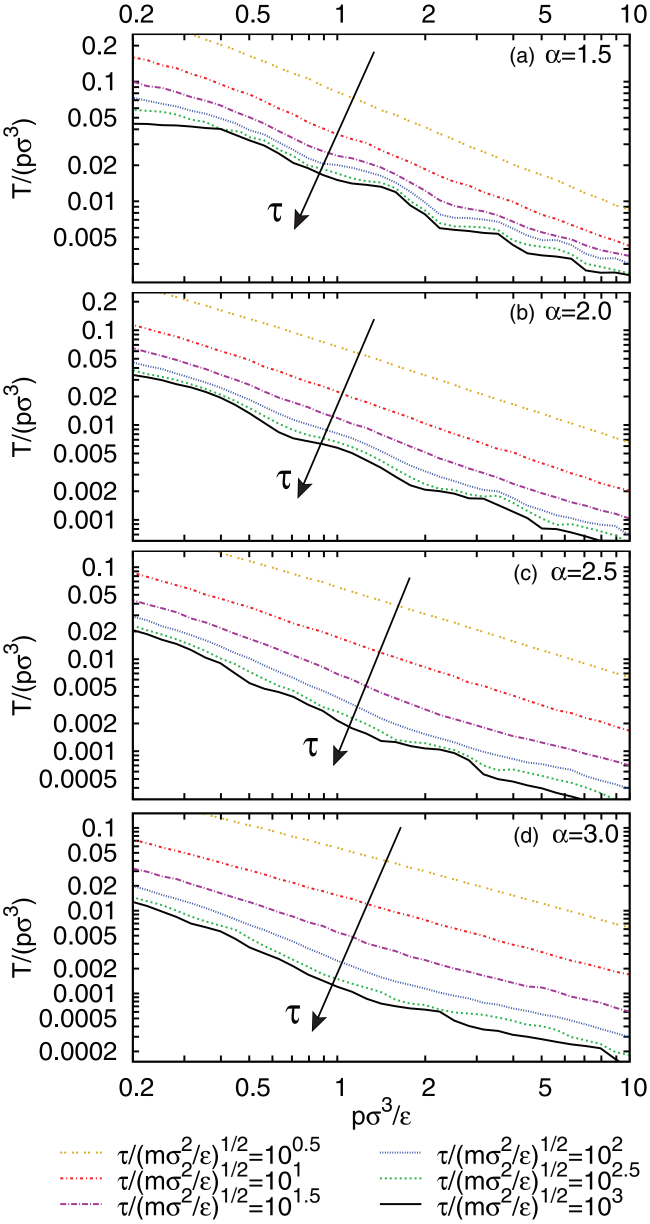

FIG. 5. (Color online) Jamming phase diagrams depending on temperature over pressure T/p and pressure p. Time is given in units of $(m\sigma^2/\epsilon)^{1/2}$. The exponent of the interaction potential is (a) $\alpha = 1.5$, (b) $\alpha = 2$, (c) $\alpha = 2.5$, and (d) $\alpha = 3$.

Figure 6(a) shows a comparison of the lines with relaxation time $\tau = 1000\sqrt{m\sigma^2/\epsilon}$ for different exponents α. As shown previously [7,9], such lines should originate from the universal hard-sphere limit for $p \to 0$. However, for the pressures or densities studied here, we already observe significant

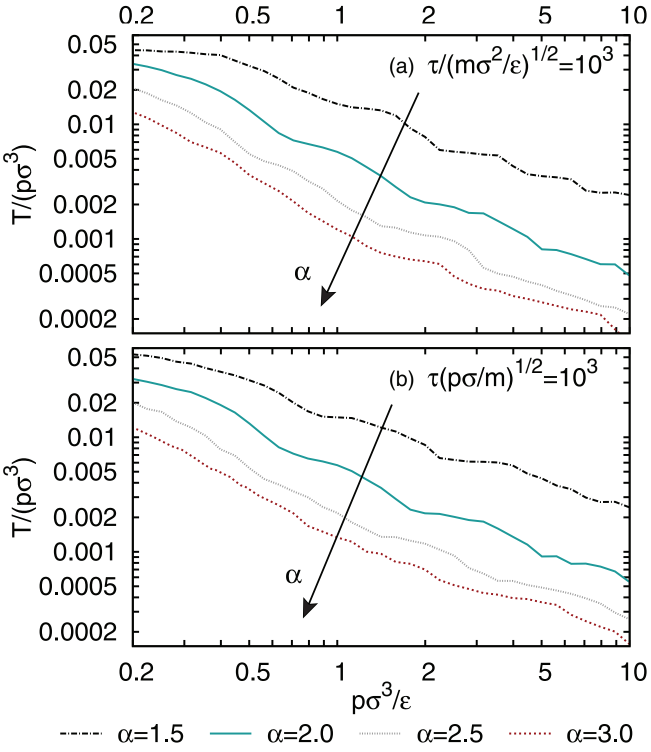

FIG. 6. (Color online) Comparison of lines with constant relaxation time (a) $\tau = 1000\sqrt{m\sigma^2/\epsilon}$ and (b) $\tau = 1000\sqrt{m/(p\sigma)}$ for different exponents α. Temperature over pressure T/p and pressure p are used as control parameters. Note that (a) and (b) differ by the employed unit of time.

differences between the curves for different α. In particular, in systems with soft spheres, i.e., large α, the relaxation times are smaller than in systems with small α that are closer to the hard-sphere limit.

For completeness we also determined the new jamming phase diagrams for lines of constant relaxation times where the time is given in units of $\sqrt{m/(p\sigma)}$ instead of in units of $\sqrt{m\sigma^2/\epsilon}$. In Fig. 6(b) we plot the lines with $\tau = 1000\sqrt{m/(p\sigma)}$ for different exponents α as a function of the new control parameter. The differences between the different employed time units are small. Though for $\sqrt{m/(p\sigma)}$ as a unit of time there are some almost horizontal parts in the lines of constant relaxation time, we did not observe any nonmonotonous curves for all parameters we looked at.

VII. CONCLUSIONS

We have studied the multiple reentrant glass transitions that occur in soft-sphere systems when increasing the density. We determined the jamming phase diagrams in their traditional formulation with temperature and density as control parameter as well as in the new formulation where the lines of constant relaxation times are plotted as functions of temperature over pressure and pressure. While in the traditional diagrams the reentrant glass transitions lead to nonmonotonous lines of constant relaxation time, in diagrams employing the new set of control parameters we did not find any nonmonotonicity.

In experiments (see, e.g., [4]) the density or packing fraction are accessible parameters, while the pressure probably is hard to determine. Therefore, the traditional jamming phase diagrams seem to be the obvious choice for experimentalists. However, from a theoretical point of view, the new set of control parameters possesses important advantages. In the limit $p \rightarrow 0$ the universal hard-sphere limit is obtained [7,8] for all repulsive, finite-ranged interaction potentials. Furthermore, while for the traditional control parameters any pertubative approximation that is employed in order to connect the relaxation times for different densities or for different interactions seems to be hard to apply, such approximations are more likely to work in terms of pressure and temperature over pressure. As already shown in [9], the dynamics of soft spheres with small overlaps can be mapped onto the hard-sphere behavior by introducing an effective diameter using the Andersen-Weeks-Chandler approximation [26]. Probably, similar mappings can be found for larger pressures by employing methods that were developed to describe the structure of liquids at high densities (see, e.g., [27,28]). For example, the approximative description of the structure was extended to larger densities by mapping the soft-sphere system onto a soft r^{-12} reference system instead of onto hard spheres [28]. In general, since even for large overlaps the relaxation time is a monotonous function of the new control parameters and there seems to occur no dynamical crossover or any other fundamental change in the type of dynamics when the pressure is increased, we also expect that approximations used to compare the dynamics at different densities or of particles with different interactions work in a similar way as the Andersen-Weeks-Chandler approximation does close to the hard-sphere limit. Another interesting question for future research is whether scaling relations that were reported for soft spheres with small overlaps (e.g., [5,6]) can be connected to relations observed for soft spheres at high densities [12].

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