

## Transition state theory and the dynamics of hard disks

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The dynamics of two- and five-disk systems confined in a square has been studied using molecular dynamics simulations and compared with the predictions of transition state theory. We determine the partition functions  $Z$  and  $Z^\ddagger$  of transition state theory using a procedure first used by Salsburg and Wood for the pressure. Our simulations show this procedure and transition state theory are in excellent agreement with the simulations. A generalization of the transition state theory to the case of a large number of disks  $N$  is made and shown to be in full agreement with simulations of disks moving in a narrow channel. The same procedure for hard spheres in three dimensions leads to the Vogel-Fulcher-Tammann formula for their alpha relaxation time.

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### I. INTRODUCTION

The long relaxation times seen in supercooled liquids have long been a challenge to understand [1,2]. Glassy behavior has been extensively modeled by studying hard spheres in three dimensions and hard disks in two dimensions. Some of this work is reviewed in Ref. [3]. In this paper we study small systems of disks, in particular two and five disks confined in a square, first using event-driven molecular dynamics and then by means of transition state theory [4,5]. In the final section of the paper we use the insights gained from studying small systems to speculate about the behavior of large numbers of hard spheres or disks.

It is convenient from the outset to introduce the following terminology. The transition state is the neck in configuration space through which the system has to pass to escape its initial state. A *configuration* of the  $N$  disks is defined by the  $Nd$  coordinates of the disk centers (for disks,  $d = 2$ ); every configuration belongs to a *state*, which is the set of configurations that can be reached from it without violating the no-overlap constraint appropriate for hard disks and spheres. The transition state theory will be found to work well when the neck is narrow, that is, when there are long relaxation times in the system.

We shall illustrate the process of escape from the initial configuration for two simple systems, consisting of either two or five disks confined in a square. For these simple systems we can make explicit the narrow necks in configuration space through which the system can escape from its initial configuration near an inherent state [6]. We shall show that transition state theory provides a quantitative account of the slow relaxational processes in these small systems. The theory requires that one evaluates a variant of the partition function of the system at the neck ( $Z^\ddagger$ ), and to do this we adopt the procedure first used by Salsburg and Wood [7] to calculate the pressure of hard spheres near their largest packing density. We have checked its accuracy for these small systems by comparing its predictions for the pressure of the system and the relaxation times with results obtained directly from event-driven molecular dynamics.

Of course, one is only interested in small systems of disks because of the light their study might shine on large systems of hard disks or spheres. We shall show that as  $N$ , the number of disks or spheres, becomes large, then, under certain

circumstances, our transition state formula for the relaxation time in the system goes over to the well-known Vogel-Fulcher-Tammann (VFT) equation. These circumstances are evidently realized in at least one case, that of disks moving in a narrow channel [8–10]. The agreement is quantitative in this case [11]. For hard spheres in three dimensions their alpha relaxation time can be fitted by the VFT form [12], but with the divergence occurring at a density below that of random close packing. This matter is discussed in Sec. V, where we then go on to give a speculative extension to our procedure, which leads to a generalized VFT formula where the divergence takes place at a density similar to that of random close packing.

Throughout our study of two and five disks confined in a square,  $L$  denotes the length of one side of the square and  $r$  denotes the radius of the disks. The packing fraction  $\phi$  is then defined as the fraction of the area of the square that is covered by the disks,  $\phi = N\pi r^2/L^2$ . The two-disk system is studied in Sec. II. In Sec. III the inherent states and the necks in configuration space which separate them are discussed for the five-disk system. In Sec. IV we compare the results of our event-driven molecular dynamics simulations for five disks with the predictions of transition state theory.

### II. THE TWO-DISK SYSTEM

Two disks confined to a square have been considered previously by Speedy [13]. For  $r < L/4$  (or  $\phi < \phi_{\text{Neck}} \simeq 0.3927$ ) the disks can pass each other, though this becomes more difficult as  $r \rightarrow L/4$  (see Fig. 1). Awazu [14] studied an autocorrelation function which developed a plateau in this limit, and which he argued showed similarities with the  $\alpha$  and  $\beta$  relaxation processes found in glasses. For larger values of  $r$ , the configuration space (disregarding the identity of the disks) is broken into two states. For  $r \rightarrow L/(2 + \sqrt{2})$ , or  $\phi \rightarrow \phi_J \simeq 0.5390$ , the maximum density possible, the disk centers lie on the same diagonal of the square. These (two) limiting configurations are the *inherent structures* introduced in Ref. [6].

Speedy [13] has considered the thermodynamics of this system and, in particular, finds weakly nonanalytic contributions to the thermodynamic quantities, such as the pressure, at  $r = L/4$ . Speedy used transition state theory to determine the alpha relaxation time of the system, which according to

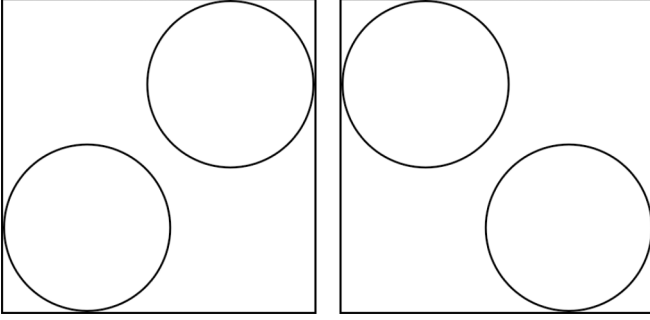


FIG. 1. Mutually inaccessible configurations of a system of two disks, illustrated for  $r = 0.27L$ , which is greater than the critical value  $r = 0.25L$  below which the disks can pass each other.

Awazu is the time  $\tau$  to flip between the two configurations. The origin of this behavior can be obtained from transition state theory [4,5]. In this well-studied approximation, which works best when the transition rate over a barrier is small, the transition rate  $R$  between two states varies as

$$R = 1/\tau \sim v \frac{Z^\ddagger}{Z}, \quad (1)$$

where  $v$  is a typical particle speed and  $Z^\ddagger$  is the partition function evaluated at the top of the barrier along the trajectory which separates the states; see Ref. [5] for a full description of the transition state formalism and the definition of  $Z^\ddagger$ . In the case of two disks passing this means that instead of the full partition function integral over  $(x_1, y_1)$  and  $(x_2, y_2)$ , there is a constraint that  $y_1 = y_2 \equiv y$ , so it is effectively a three-dimensional integral. The integral over  $y$  gives a trivial factor  $(L - 2r)$ , and the remaining two integrals give a factor  $(1 - \phi/\phi_{\text{Neck}})^2$  in the limit  $\phi \rightarrow \phi_{\text{Neck}}$  by the argument used by Salsburg and Wood [7].  $Z$  itself is essentially just a constant:

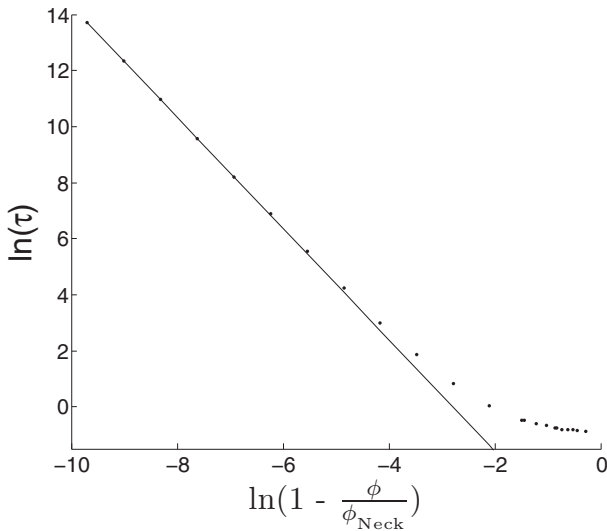


FIG. 2. Molecular dynamics transition rates ( $1/\tau$ ) between metastable “glassy” states of the two-disk system, as the packing fraction,  $\phi$ , approaches the critical value  $\phi_{\text{Neck}} \simeq 0.3927$  corresponding to  $r = 0.25L$ . The gradient of the straight-line fit to the last five points is  $-1.986$ , which is close to the value  $-2$  predicted by transition state theory.

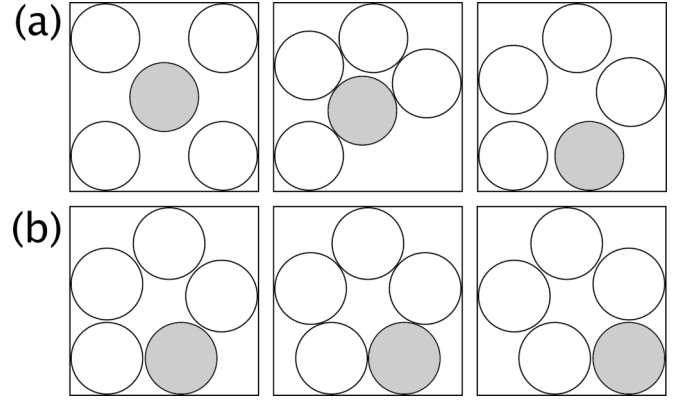


FIG. 3. (a) Representative configurations of the “crystalline” (left) and “glassy” (right) states of a five-disk system, connected by a transition state (center), shown here with the largest radius,  $r \simeq 0.1863L$ , for which the transition between crystalline and glassy states is possible; (b) two frozen glass states (left and right) and the transition state (center) connecting them, shown with the maximum radius,  $r \simeq 0.1942L$ , for which a transition between glass states is possible.

it has a very mild singularity,  $Z_{\text{reg}} + C(1 - \phi_{\text{Neck}}/\phi)^{5/2}$ , when the packing fraction  $\phi$  approaches  $\phi_{\text{Neck}}$  from above [13]. Transition state theory thus predicts a slope of  $-2$  in Fig. 2 for the dependence of the relaxation time on packing fraction as  $\phi \rightarrow \phi_{\text{Neck}}$ . (The full integrals for  $Z^\ddagger$  and  $Z$  were explicitly evaluated by Speedy [13].) Our event-driven molecular dynamics results (Fig. 2) are consistent with the transition state theory prediction that  $\tau \sim 1/(1 - \phi/\phi_{\text{Neck}})^\alpha$ , with  $\alpha = 2$ , for the case of two disks in a square box, in the limit  $\phi \rightarrow \phi_{\text{Neck}}$ .

### III. CONFIGURATIONS OF THE FIVE-DISK SYSTEM

The configuration space of five disks confined to a square has been analyzed previously: Bowles and Speedy [15] have discussed the thermodynamics and dynamics; Hinow [16] has studied the jammed states of this system; and Carlsson *et al.* [17] have given a detailed analysis of how the topology of the configuration space depends on  $r$ . We refer to Fig. 3 for configurations of the disks at two critical values of the radius.

Below the fluid-crystal critical point, i.e., for  $r < r_{\text{cg}} \simeq 0.1863L$ , the system is fluid (any pair of disks can exchange position), but for slightly greater values of  $r$  the configuration space is fractured into two states: a “crystal” state in which one disk is surrounded by the four others, confined near the corners of the box, and a “glass” state in which all five disks lie close to the walls of the box and are unable to change their order. Above  $r = r_{\text{gg}} \simeq 0.1942L$ , the glass state fractures further into four “frozen” glass states of the kind illustrated in Fig. 3(b), in which one disk is confined near a corner of the box. Above  $r = r_g \simeq 0.1964L$ , the system can exist only in the crystalline state.

It may be noticed that  $r_{\text{cg}} \simeq 0.1863L$  differs significantly from the value  $0.1871$  stated by Carlsson *et al.* [17]. We have been unable to find a path between glasslike and crystal-like metastable states that passes via the configuration proposed in their paper. We find, moreover, that their proposed state with  $r \simeq 0.1871L$  is not a stationary point of the softened

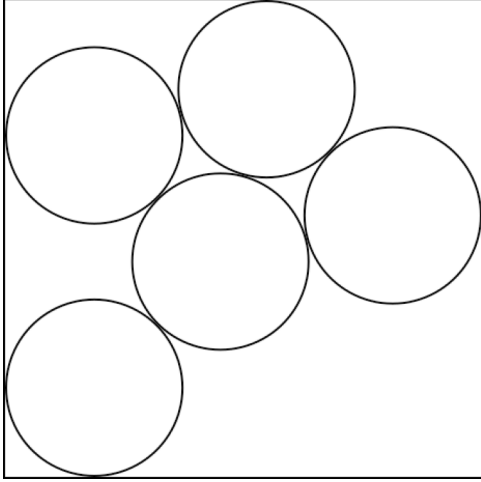


FIG. 4. The dead-end configuration at  $r \simeq 0.1871L$ , which has been incorrectly identified as a saddle point in Refs. [16,17].

potential energy function  $E$  introduced in Ref. [17]: instead, it is a minimum of  $|\nabla E|^2$  at which  $\nabla E \neq 0$ . It is a dead-end configuration, illustrated in Fig. 4: it can be reached from the crystal by the steps in the first two panels of Fig. 3(a), but progress to the glass state of the third panel is not possible as the central disk cannot escape to the edge of the square. On the other hand, we can show that our own configuration at  $r \simeq 0.1863L$  lies on a path between crystal-like and glass-like states and also that this configuration corresponds very precisely to an ordinary saddle point of  $E$ . Such a reaction path is illustrated by an animation provided in the supplement to this paper [18].

#### IV. DYNAMICS OF THE FIVE-DISK SYSTEM

As for the case of two disks, an event-driven molecular dynamics algorithm [19] was used to simulate the motion of the five-disk system and calculate the mean time of passage between metastable states. The initial velocities of the disks were drawn from the Maxwell-Boltzmann distribution.

A very simple method was used in our work to identify when a transition had taken place. For the transition from crystal to glass states, the simulation is started in a typical ‘‘crystal’’ configuration with one disk [Fig. 3(a), shaded] near to the center of the box. The shaded disk’s first collision with any wall is an unambiguous sign that the transition to the glass state has occurred. Transitions between metastable glass states can be identified in a similar way. From Fig. 3(b), we can see that a transition has occurred if a disk [e.g., the shaded disk in Fig. 3(b)] makes a collision with a wall other than the one it was close to in the initial configuration. For each kind of transition, the time of first occurrence of the diagnostic event is recorded and the simulation restarted with random initial velocities.

Transition state theory requires us to evaluate  $Z^\ddagger$  and  $Z$ . We shall use the procedure introduced by Salsburg and Wood [7] to determine these as it becomes essentially exact as the density approaches its maximum value (called  $\phi_J$ ) appropriate for a given inherent state. Thus for the crystal state  $r_c = 0.2071L$ , so  $\phi_J = 5\pi r_c^2/L^2 \approx 0.6738$ . Let  $l = (V/N)^{1/d}$  denote the

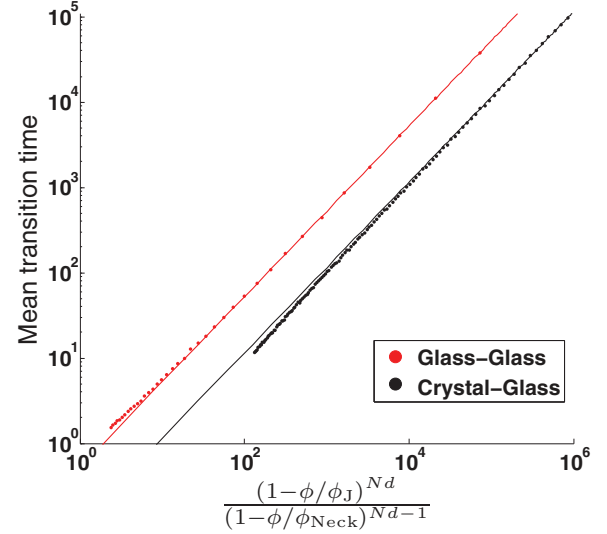


FIG. 5. (Color online) Transition times between pairs of metastable states. Results from molecular dynamics are compared to the predictions of transition state theory for transitions between (1) two glass states just below the ‘‘glass-glass’’ transition, where  $\phi_J = 0.6061$  and  $\phi_{\text{Neck}} = 0.5925$ ; and (2) the crystalline and glass states, where  $\phi_J = 0.6738$  and  $\phi_{\text{Neck}} = 0.5453$ . In each case  $N = 5$  and  $d = 2$ . The error bars for the molecular dynamics results are comparable with the size of the data points.

average spacing between the centers of the particles, where  $V = L^d$ . The Salsburg-Wood approximation is that as  $\phi \rightarrow \phi_J$ ,  $Z \sim l^{Nd}(1 - \phi/\phi_J)^{Nd}$ , where here  $N = 5$ ,  $d = 2$ . Similarly, as  $\phi \rightarrow \phi_{\text{Neck}}$  from below,  $Z^\ddagger \sim l^{Nd-1}(1 - \phi/\phi_{\text{Neck}})^{Nd-1}$ , where  $\phi_{\text{Neck}} = 0.5453$ . Hence, according to transition state theory, the transition rate  $R$  from the crystal to the glass state should vary as

$$R = 1/\tau \sim \frac{v}{l} \frac{(1 - \phi/\phi_{\text{Neck}})^{Nd-1}}{(1 - \phi/\phi_J)^{Nd}}. \quad (2)$$

If the reaction coordinate is fixed at the value it takes in the transition state, the hard-disk constraints define a configuration space with nine spatial dimensions in our two-dimensional hard disk system. Accordingly, the constrained partition function should be expected to vary as  $(1 - \phi/\phi_{\text{Neck}})^9$  using the procedure of Salsburg and Wood [7].

Our simulations to test this for both the glass glass transition and the crystal glass transition are plotted in Fig. 5. The agreement is excellent as  $\phi \rightarrow \phi_{\text{Neck}}$ .

To further examine the accuracy of the Salsburg-Wood procedure for calculating  $Z$  and  $Z^\ddagger$ , we have determined from our molecular dynamics simulations the pressure of the system in the glass states. The temperature was obtained from the average kinetic energy, using  $k_B T = m\langle v^2 \rangle/2$ . The results are shown in Fig. 6. The Salsburg-Wood approximation for  $Z$  predicts that the pressure

$$\frac{PV}{Nk_B T} = 1 + d \frac{\phi}{\phi_J - \phi}, \quad (3)$$

on using the relation  $P = k_B T \partial \ln Z / \partial V$ . The straight line in Fig. 6 represents the prediction of the Salsburg-Wood

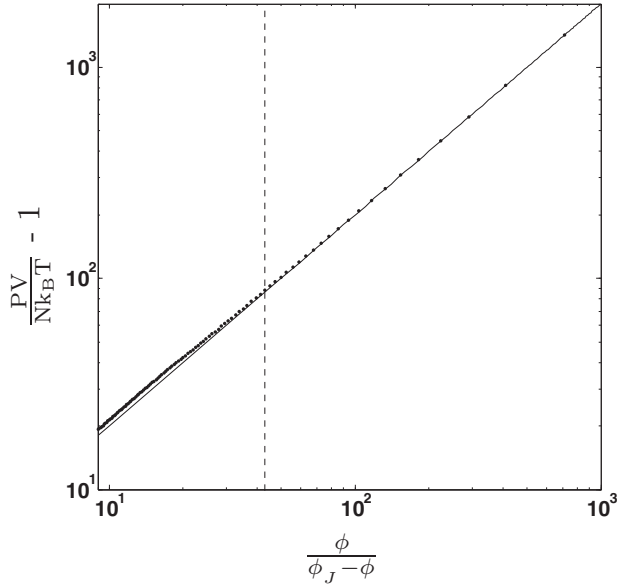


FIG. 6. Pressure in the glass states. For the glass states, the maximum possible packing fraction is at  $\phi_J = 0.6061$ . The packing fraction at the neck  $\phi_{\text{Neck}} = 0.5925$  separates the two kinds of glassy state and is marked by the dashed vertical line. The glass phase exists only down to a packing fraction 0.5432 as a stable state and only data obtained above this value are included. The straight line is Eq. (3).

calculation for the pressure, i.e., Eq. (3), and is in perfect agreement with the data as  $\phi \rightarrow \phi_J$ . Notice that at the neck,  $\phi = 0.5925$ , which is indicated by the vertical dashed line in Fig. 6, the singularities are so mild as to be invisible, which means it is adequate to use in Eq. (2) the form of  $Z$  valid near  $\phi_J$ , even for  $\phi$  close to  $\phi_{\text{Neck}}$ . (Also, the expression for  $\tau$  is dominated by the form of  $Z^{\frac{1}{2}}$ , which is rapidly approaching zero as  $\phi \rightarrow \phi_{\text{Neck}}$ , while  $Z$  is there only slowly varying.)

## V. LARGE NUMBERS OF SPHERES OR DISKS

In our studies of two and five disks we found that a transition between states in a region containing  $N$  particles generally requires coordinated motion of all the  $N$  particles in order to squeeze through the neck in the phase space. The rate at which this will occur was given by the transition state formula of Eq. (2). In this section we examine the consequences of assuming that the formula can be extended to systems containing a large number  $N$  of spheres or disks.

We shall first suppose that one is at a packing fraction below that of the neck out of an inherent state whose largest density is at a packing fraction  $\phi_J$  and that  $\phi_{\text{Neck}}$  is the highest packing fraction below  $\phi_J$  at which a neck first opens to allow escape from the inherent state, and that one is in a configuration close to that of the inherent state. Furthermore we shall assume that when  $N$  is large,

$$\phi_J - \phi_{\text{Neck}} = a\phi_J/N, \quad (4)$$

where  $a$  is a positive constant of  $O(1)$ . The assumption behind Eq. (4) is that escape from a jammed state will become possible if the volume of the system is increased by an amount of the order of the volume of a single sphere. With this assumption,

and taking  $N$  to be large, Eq. (2) reduces to

$$\frac{1}{\tau} = \frac{1}{\tau_0} \left[ 1 - \frac{a\phi}{(1 - \phi/\phi_J)\phi_J N} \right]^{Nd-1}, \quad (5)$$

where  $\tau_0 = l(1 - \phi/\phi_J)/v$  denotes the typical time between collisions of the disks. Then as  $N \rightarrow \infty$ ,

$$\tau = \tau_0 \exp \left[ \frac{ad\phi}{(\phi_J - \phi)} \right], \quad (6)$$

which is the Vogel-Fulcher-Tammann formula.

Given a particular configuration of the  $N$  particles with a packing fraction  $\phi$  we need to know the packing fraction  $\phi_J$  of the nearby inherent state close to the initial configuration. In other words, we need the Stillinger map to the jammed inherent states [10,20]. For the problem of disks moving in a long narrow channel such a map was explicitly constructed in Ref. [10] and the function  $\phi_J(\phi)$  exhibited. Except for quite small values of  $\phi$ ,  $\phi_J(\phi)$  is essentially a constant independent of  $\phi$  and close to the largest packing fraction possible in the system. The map is similar to what would have been obtained in an extremely rapid compression. The relaxation times  $\tau$  in this narrow channel system are consistent with Eq. (6) [8]. It has proved possible to identify the inherent states and the necks which have to be squeezed through to escape from the vicinity of the inherent states, and as a consequence the value of the coefficient  $a$  can be explicitly determined for this system [11].

In dimensions  $d > 1$  much less can be said with certainty. Fits of the alpha relaxation time to the VFT formula for three-dimensional hard spheres were made by Brambilla *et al.* [12], and a fit was achieved with a value of  $\phi_J \approx 0.615$ . One might have expected that the appropriate value of  $\phi_J$  if the map from  $\phi$  to the inherent state is essentially a rapid compression would be that of random close packing,  $\phi_{\text{rcp}} \approx 0.64$ . The result that  $\phi_J \approx 0.615$  was obtained for studies of  $\tau$  at  $\phi \leq 0.6$ , and it might require data at larger values of  $\phi$  to produce  $\phi_J$  values closer to  $\phi_{\text{rcp}}$ .

We have been assuming that the Stillinger map in two and three dimensions,  $\phi_J(\phi)$ , is essentially a constant independent of  $\phi$ . This lack of any  $\phi$  dependence of  $\phi_J(\phi)$  seems unlikely according to the studies in Refs. [21,22]. Suppose that instead the Stillinger map in two and three dimensions takes the form, for  $\phi$  close to  $\phi_{\text{rcp}}$ ,

$$\phi_J(\phi) \approx \phi + B(\phi_{\text{rcp}} - \phi)^\delta, \quad (7)$$

with  $B > 0$ . To test this supposition, one would need to start the rapid compression from the well-equilibrated fluid system at a packing fraction near  $\phi_{\text{rcp}}$ . Producing this initial state would be difficult. If Eq. (7) is valid, it would lead to the following expression for the alpha relaxation time:

$$\tau_\alpha(\phi) = \tau_0 \exp \left[ \frac{A}{(\phi_{\text{rcp}} - \phi)^\delta} \right]. \quad (8)$$

In Ref. [12], a good fit was obtained with  $\delta = 2$  and a value for  $\phi_{\text{rcp}} \approx 0.64$ , a commonly quoted value.

In words, Eq. (7) states that if one starts from the equilibrated system at a packing fraction  $\phi$  close to  $\phi_{\text{rcp}}$ , then the rapid compression (or the Stillinger map) finds a jammed state whose packing fraction  $\phi_J$  differs from  $\phi$  only by a quantity of order  $(\phi_{\text{rcp}} - \phi)^\delta$ , which is small when  $\delta > 1$ . The

physical implication is that equilibrated systems at such high densities are always close to a jammed state. However, Eq. (7) also assumes that  $\phi_{\text{rcp}}$  is a well-defined density, and this is contentious [23]. Notice that our difficulties in using Eq. (6) stem from just not knowing the form of the Stillinger map  $\phi_J(\phi)$  for two- and three-dimensional systems. It is possible that it takes a form that would leave  $\tau_\alpha$  finite for all  $\phi$  less than that of the maximum density. In this situation it could be that for  $\phi$  well below  $\phi_{\text{rcp}}$   $\tau_\alpha$  might appear to be diverging as  $\phi \rightarrow \phi_{\text{rcp}}$ , but if studies could be performed nearer  $\phi_{\text{rcp}}$  the relaxation times would be very long but finite.

In conclusion we have shown that the long relaxation times seen in small systems of two and five disks confined in a square are due to squeezing through necks in configuration space, and can be understood quantitatively with the aid of transition state theory. We have suggested that a similar mechanism might be relevant to hard spheres in higher dimensions and could lead either to the VFT formula or possibly a generalization of it.

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