Diverging Time Scale in the Dimensional Crossover for Liquids in Strong Confinement

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(Received 22 June 2016; published 6 February 2017)

We study a strongly interacting dense hard-sphere system confined between two parallel plates by event-driven molecular dynamics simulations to address the fundamental question of the nature of the 3D to 2D crossover. As the fluid becomes more and more confined the dynamics of the transverse and lateral degrees of freedom decouple, which is accompanied by a diverging time scale separating 2D from 3D behavior. Relying on the time-correlation function of the transversal kinetic energy, the scaling behavior and its density dependence is explored. Surprisingly, our simulations reveal that its time dependence becomes purely exponential such that memory effects can be ignored. We rationalize our findings quantitatively in terms of an analytic theory which becomes exact in the limit of strong confinement.

DOI: 10.1103/PhysRevLett.118.065901

Introduction.—Transport of particles in nanoconfinement is of great scientific and industrial importance, with applications in heterogeneous catalysis [1], oil recovery [2], or lubrication [3–6]. In recent years artificial nanoporous materials such as metal organic frameworks [7,8], zeolites [9,10], and biocompatible scaffolds [11] have also triggered many novel applications, including gas storage [12], repairing or regenerating tissues [11], size-selective molecular sieving [13], lab-on-a chip technology, and nanofluidics [14,15]. The efficiency of such nanodevices often crucially depends on higher surface to volume ratio, such that the distance between the confining walls may even reach atomic scale [16], or the system effectively becomes quasi-2D. Nevertheless, despite its long history, a deep understanding of the transport mechanisms in nanoconfinement and how the dimensional crossover occurs dynamically is still far from satisfactory.

Early theoretical studies on transport in nanoconfinement starting from Knudsen [17] and Smoluchowski [18] focused on dilute hard-sphere gases where exact results could be obtained analytically in the low-density limit [17–22] by assuming particle-wall collisions as diffusive. In contrast, confinement effects on dense strongly interacting systems have only recently come into focus [23]. There, the simplest geometry to investigate the effects of strong confinement is a slit where fluid particles are restricted to a narrow space between two smooth parallel plates, but also tubes or spherical confinements have been realized experimentally [24–26]. Computer simulations and experiments for the planar confinement have revealed an exotic equilibrium phase behavior due to commensurable stacking [27–34] as well as the hexatic phases in the limit of quasi-2D confinement [35,36]. Confinement induced order-disorder phase transitions for certain nonpolar liquids have also been reported in several experiments [37], but the interpretation has been challenged in favor of a glass transition [38–40]. The structural properties of strongly confined liquids have been measured directly only recently by x-ray scattering [41,42].

The structural changes by the confinement also have drastic ramifications for the dynamic properties. For instance, the role of local order has been elucidated within a remarkable empirical scaling of the diffusivity or structural relaxation times with the excess entropy [43–46]. Complementarily, a microscopic theory for the dynamics in confinement is the mode-coupling theory that predicts a multiple reentrant in a glassy phase as the plate separation is varied [33,47,48].

From a more fundamental point of view, one would like to know how the dimensional crossover from a 3D bulk liquid to a (quasi-)2D system occurs. For the thermodynamic and structural properties, it has been shown recently that a small parameter emerges such that the convergence to a 2D system including leading corrections can be proven [49]. The key observation there was that in strong confinement the canonical ensemble for the fluid in a slit geometry decouples into a two-dimensional fluid in the lateral plane and an ideal gas in the transversal direction. However, the consequences of the weak coupling between lateral and transversal degrees of freedom for slow equilibration and how time-dependent correlation functions will be affected by coupling to the "other dimension" have remained mostly unexplored.

In this Letter, we now address the dynamical confinement problem and demonstrate that as the fluid becomes more and more confined, a singular time scale emerges separating 2D from 3D behavior. The dependence of this divergent time scale on the plate separation and the packing fraction will be worked out analytically including the prefactor and validated by simulations.

Simulation.—We investigate a fluid of hard spheres of diameter σ confined between two flat parallel hard walls with accessible slit width L; see Fig. 1. Trajectories are computed by event-driven molecular dynamics with initial

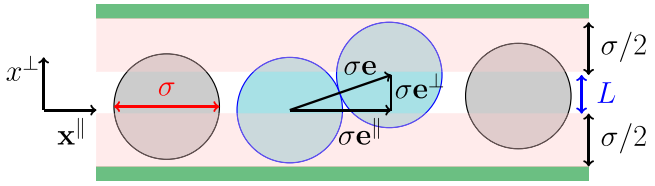

FIG. 1. Schematic cross section of hard spheres of diameter σ confined to a slit of accessible width L. For two colliding spheres the velocity transfer is directed along the connecting vector $\sigma\mathbf{e}$, which lies almost parallel to the walls for small widths L.

velocities drawn from a Maxwell-Boltzmann distribution with thermal velocity $v_{\mathrm{th}} = \sqrt{k_B T/m}$, which also sets the natural time scale $t_0 = \sigma/v_{\mathrm{th}}$. We focus on small wall separations $L/\sigma = 0.01, \ldots, 0.5 < 1$ such that only a single monolayer fits between the plates and consider systems at 2D packing fractions $\varphi_{2\mathrm{D}} = (\pi/4)\sigma^2 N/A = 0.1, \ldots, 0.8$ for N particles per area A, such that the highest densities are already beyond the freezing transition.

To unravel the divergent time scale, we choose an observable that displays nontrivial dynamics exclusively due to the weak coupling of the transversal to the lateral degrees of freedom. Since in the decoupled ensemble the lateral degrees of freedom evolve just like in a confined ideal gas, a natural candidate is the transversal kinetic energy $\epsilon_s^\perp(t) = (m/2)[v_s^\perp(t)]^2$ of a tagged particle, i.e., any $s \in \{1, \ldots, N\}$, and $v_s^\perp(t)$ is the fluctuating velocity perpendicular to the plates. We therefore monitor the time-correlation function,

$$T_s^\perp(t) = \langle \delta\epsilon_s^\perp(t)\delta\epsilon_s^\perp(0)\rangle, \tag{1}$$

of the fluctuations $\delta\epsilon_s^\perp(t) = \epsilon_s^\perp(t) - k_B T/2$. From the Maxwell-Boltzmann distribution one readily computes its initial value, $T_s^\perp(0) = \langle|\delta\epsilon_s^\perp|^2\rangle = (k_B T)^2/2$.

The simulation results are displayed in Fig. 2(a) for the moderate packing fraction $\varphi_{2\mathrm{D}} = 0.4$ (well below the two-dimensional freezing transition to a triangular phase $\varphi_{2\mathrm{D}}^{\mathrm{freezing}} \approx 0.69$ [27,29,49]) for accessible plate separations covering two decades. One infers that the characteristic time scale increases by 4 orders of magnitude as the plate separation is decreased by a factor of 100, while the shape of the relaxation function becomes independent of the plate distance for small L. This suggests that data collapse can be achieved upon proper rescaling with the measured relaxation time. Plotting the data on a semi-log plot then demonstrates that for small L the data follow a pure exponential $\exp(-t/\tau)$ even at the smallest time scales; see Fig. 2(b). Deviations become apparent only at the largest distance considered, $L/\sigma = 1$.

The relaxation times $\tau = \tau(L, \varphi_{2\mathrm{D}})$ extracted from the simulations, see Fig. 3, approach a divergence $\sim L^{-2}$ for all packing fractions considered, the power law being an excellent description of the data already at wall separations $L/\sigma \lesssim 0.5$. Dimensional analysis suggests that in this regime the relaxation rate should read

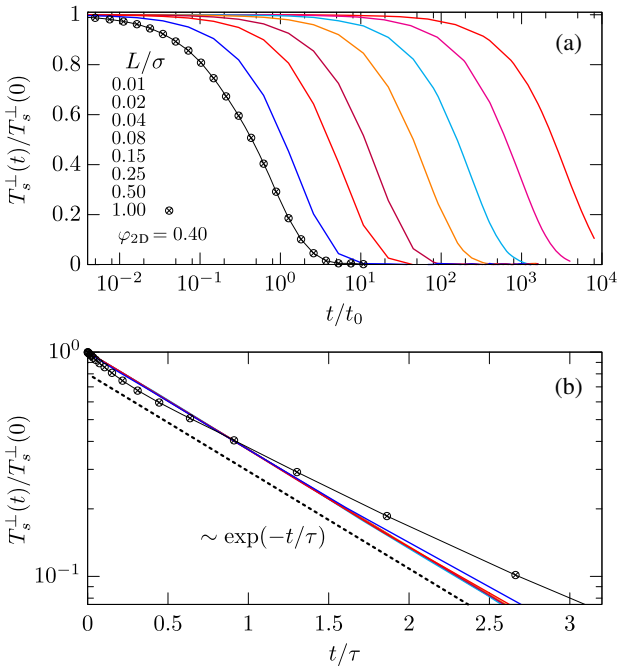

FIG. 2. (a) Decay of the time-correlation function $T_s^\perp(t)$ of the transversal kinetic energy for $\varphi_{2\mathrm{D}} = 0.40$ and various wall separations L. Wall distance decreases from left to right. (b) Same data in semi-log plot after rescaling with the measured relaxation time τ. As a guide to the eye, the dashed line indicates a pure exponential decay, $\sim\exp(-t/\tau)$.

$$\tau^{-1} = t_0^{-1}\left(\frac{L}{\sigma}\right)^2 A(\varphi_{2\mathrm{D}}), \tag{2}$$

where the prefactor $A(\varphi_{2\mathrm{D}})$ depends on the packing fraction only. The prefactors $A(\varphi_{2\mathrm{D}})$ as measured from the simulation data, displayed in Fig. 4, increases smoothly with the packing fraction; in particular, it grows stronger than the packing fraction itself.

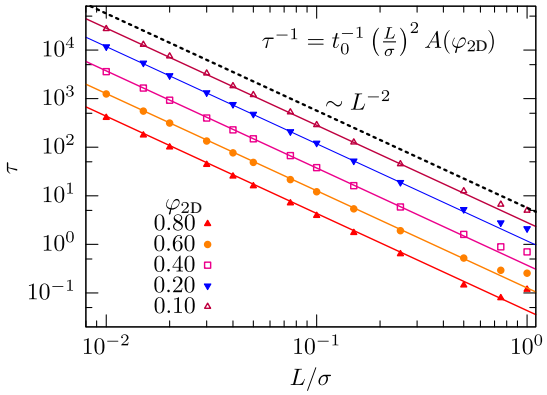

FIG. 3. Relaxation time τ for the strongly confined liquids as a function of the wall separation L for various packing fractions $\varphi_{2\mathrm{D}}$. Packing fraction increases from top to bottom. The dashed line is a power law $\sim L^{-2}$ and serves as a guide to the eye.

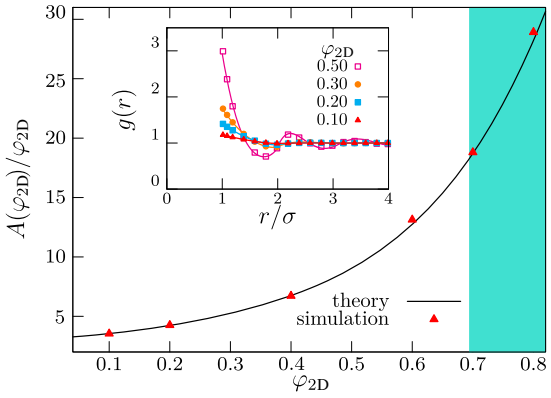

FIG. 4. Prefactor $A(\varphi_{2D})$ for the scaling behavior of the relaxation rate $\tau(L,\varphi_{2D})^{-1} = t_0^{-1}(L/\sigma)^2 A(\varphi_{2D})$ as a function of 2D packing fraction φ_{2D}. The shaded area indicates the ordered phase. The inset shows the 2D radial distribution function at some representative packing fractions. The solid lines are from the Ornstein-Zernike relation using the Percus-Yevick closure, whereas the symbols are from simulations.

Theory.—The coordinates and velocities of the particles split naturally into lateral and transversal degrees of freedom, $\mathbf{x}_n = (\mathbf{x}_n^{\parallel}, x_n^{\perp})$, $\mathbf{v}_n = (\mathbf{v}_n^{\parallel}, v_n^{\perp})$, $n = 1,\ldots,N$, and the confinement restricts the transversal coordinates to $|x_n^{\perp}| \le L/2$; see Fig. 1. The time evolution of an observable $A(t) = A(\{\mathbf{x}_n(t)\},\{\mathbf{v}_n(t)\})$ is inherited from the trajectories and is formally encoded in $A(t) = \exp(i\mathcal{L}_{\pm}t)A$, $t \gtrless 0$, with the pseudo-Liouville operator [50,51]

$$i\mathcal{L}_{\pm} = \sum_n \mathbf{v}_n \cdot \frac{\partial}{\partial \mathbf{x}_n} + \sum_n \hat{W}_{\pm}(n) + \sum_{m<n} \hat{T}_{\pm}(m,n). \quad (3)$$

Here, the first term describes merely the free-streaming motion, while the operator $\hat{W}_{\pm}(n)$ in the second term accounts for the collision of particle n with the hard walls. Explicit expressions are readily derived following the standard method [51] but will not be needed in the following. The interaction between the hard spheres is encoded in the binary collision operator:

$$\hat{T}_{\pm}(mn) = \sigma^2 \int d\mathbf{e}\, \Theta(\mp \mathbf{v}_{mn}\cdot\mathbf{e})|\mathbf{v}_{mn}\cdot\mathbf{e}| \times \delta^{(3)}(\mathbf{x}_{mn} - \sigma\mathbf{e})[\hat{b}^{\mathbf{e}}(mn) - 1]. \quad (4)$$

Here, $\mathbf{e}$ is a unit vector and the integral extends over the unit sphere. The normal component of the relative velocity of the colliding pair $\mathbf{v}_{mn}\cdot\mathbf{e} = (\mathbf{v}_m - \mathbf{v}_n)\cdot\mathbf{e}$ (multiplied by the infinitesimal time dt) defines the collision cylinder. The Heaviside step function $\Theta(\cdot)$ selects approaching or distancing particles and the δ function ensures the contact condition for the collision and determines the unit vector $\mathbf{e}$. The operator $\hat{b}^{\mathbf{e}}(mn)$ acts only on the velocities $\mathbf{v}_m$ and $\mathbf{v}_n$ and replaces them by the velocities $\tilde{\mathbf{v}}_m, \tilde{\mathbf{v}}_n$ after the collision:

$$b^{\mathbf{e}}(mn)\mathbf{v}_m \coloneqq \tilde{\mathbf{v}}_m = \mathbf{v}_m - \mathbf{e}(\mathbf{e}\cdot\mathbf{v}_{mn}),$$
$$b^{\mathbf{e}}(mn)\mathbf{v}_n \coloneqq \tilde{\mathbf{v}}_n = \mathbf{v}_n + \mathbf{e}(\mathbf{e}\cdot\mathbf{v}_{mn}). \quad (5)$$

The coupling between the transversal and lateral degrees of freedom occurs only via the collisions $\hat{T}_{\pm}(mn)$. Yet, if the accessible slit width is much smaller than the hard-sphere diameter, $L \ll \sigma$, the unit vector $\mathbf{e} = (\mathbf{e}^{\parallel}, e^{\perp})$ for the contact condition satisfies $|e^{\perp}| \le L/\sigma \ll 1, |\mathbf{e}^{\parallel}| \simeq 1$, see Fig. 1, such that the momentum transfer is almost planar. This insight suggests that the collision operator may be replaced to leading order by its two-dimensional analogue $\hat{T}_{\pm}^{\parallel}(mn)$, where the contact condition $\delta^{(3)}(\mathbf{x}_{mn} - \sigma\epsilon) \mapsto \delta^{(2)}(\mathbf{x}_{mn}^{\parallel} - \sigma\mathbf{e}^{\parallel})\delta(\sigma e^{\perp})$ in Eq. (4) is replaced by a collision within the plane. Then the pseudo-Liouville operator naturally decomposes,

$$i\mathcal{L}_{\pm} = i\mathcal{L}_{\pm}^{\perp} + i\mathcal{L}_{\pm}^{\parallel} + i\mathcal{L}_{\pm}^{\mathrm{int}}, \quad (6)$$

where $\mathcal{L}_{\pm}^{\perp}$ accounts for the transversal degrees of freedom of a confined ideal gas, $\mathcal{L}_{\pm}^{\parallel}$ corresponds to the time evolution of a two-dimensional hard-disk fluid, while the residual interaction is encoded in

$$i\mathcal{L}_{\pm}^{\mathrm{int}} = \sum_{m<n}[\hat{T}_{\pm}(m,n) - \hat{T}_{\pm}^{\parallel}(m,n)]. \quad (7)$$

The idea is that $i\mathcal{L}_{\pm}^{\mathrm{int}}$ induces only a weak coupling. Ignoring this contribution leads to a decoupled ensemble of interacting lateral degrees of freedom and an ideal gas of transversal degrees of freedom. This weak coupling therefore introduces a time scale up to which the coupling of the degrees of freedom is irrelevant. As the plate separation becomes smaller, this time scale is expected to grow.

The transversal kinetic energy is conserved in the decoupled ensemble $\partial_t \delta\epsilon_s^{\perp} = i\mathcal{L}_{\pm}^{\mathrm{int}}\delta\epsilon_s^{\perp}$ and the decay of its time correlation function $T_s^{\perp}(t)$ directly reflects the small coupling. Relying on the Zwanzig-Mori projection operator formalism [52,53], an exact equation of motion (e.o.m.) can be readily derived [54] for $t > 0$:

$$\dot{T}_s^{\perp}(t) + \tau^{-1}T_s^{\perp}(t) + \int_0^t K_s^{\perp}(t-t')T_s^{\perp}(t')dt' = 0. \quad (8)$$

Here, the second term describes an instantaneous relaxation, whereas the convolution integral accounts for the retarded friction due to correlated sequences of collisions. A short-time expansion of the e.o.m., Eq. (8), yields $T_s^{\perp}(t)/T_s^{\perp}(0) = 1 - t/\tau + \mathcal{O}(t^2)$, and the convolution integral over the memory kernel $K_s^{\perp}(t)$ contributes only to order $\mathcal{O}(t^2)$. Direct expansion of $\delta\epsilon_s^{\perp}(t) = \exp(i\mathcal{L}_{\pm}t)\delta\epsilon_s^{\perp}$ in powers of t in $T_s^{\perp}(t)$ yields for the relaxation rate the microscopic expression

$$\tau^{-1} = \langle \delta\epsilon_s^{\perp}(\mp i\mathcal{L}_{\pm}^{\mathrm{int}}\delta\epsilon_s^{\perp})\rangle \frac{2}{(k_B T)^2}. \quad (9)$$

For the memory kernel, a microscopic expression also follows,

$$K_s^{\perp}(t) = \langle \mathcal{Q}L_+^{\mathrm{int}}\delta\epsilon_s^{\perp}|e^{-i\mathcal{Q}\mathcal{L}_-\mathcal{Q}t}|\mathcal{Q}\mathcal{L}_-^{\mathrm{int}}\delta\epsilon_s^{\perp}\rangle \frac{2}{(k_BT)^2}, \quad (10)$$

where $\mathcal{Q}$ projects onto the subspace orthogonal to $\delta\epsilon_s^{\perp}$ and the bracket corresponds to Kubo's scalar product [52–54]. Since the memory kernel contains at least two operators $\mathcal{L}_{\pm}^{\mathrm{int}}$, which we identified as small perturbation, the retarded convolution term in Eq. (8) becomes negligible with respect to the instantaneous relaxation. Then the e.o.m. [Eq. (8)] simplifies to an exponential relaxation as leading behavior consistent with our simulation results.

The relaxation rate, Eq. (9), involves an equilibrium average of essentially the collision operator. Its direct evaluation becomes feasible for strong confinement relying on the decoupling property of the ensemble into lateral and transversal degrees of freedom, as well as the usual decoupling of the structural and kinetic degrees of freedom. The second crucial ingredient is that the unit vector $\mathbf{e} = (\mathbf{e}^{\parallel}, e^{\perp})$ for the contact condition becomes more and more confined to the planar direction, $|e^{\perp}| \leq L/\sigma \ll 1$. By the collision rule, Eq. (5), $\tilde{v}_s^{\perp} = v_s^{\perp} + e^{\perp}(\mathbf{e}\cdot\mathbf{v}_{ms})$, the transverse velocity remains almost unchanged after a collision. After performing the structural and kinetic averages, we obtain as leading contribution (see Supplemental Material [54])

$$\tau^{-1} = \frac{16\varphi_{2\mathrm{D}}}{3\sqrt{\pi}}\left(\frac{L}{\sigma}\right)^2 g(\sigma)t_0^{-1}, \quad (11)$$

where $g(\sigma)$ is the radial distribution function of the two-dimensional hard-disk fluid at contact. The factor $\varphi_{2\mathrm{D}}g(\sigma)$ accounts for the probability of a scattering event similar to Enskog's theory for bulk hard-sphere fluid [52]. In contrast to the 3D case, here it arises as an exact result valid at any packing fraction $\varphi_{2\mathrm{D}}$. The decoupling of the lateral and transversal degrees of freedom is encoded in the factor $(L/\sigma)^2$ reflecting the small momentum transfer in quasi-planar collisions.

The radial distribution function $g(r)$ can be evaluated within integral equations theory [52]. Here we rely on a numerical solution of the 2D Percus-Yevick closure relation [60] that compares quantitatively to our measured $g(r)$ in the simulation; see Fig. 4. Using the contact value $g(\sigma)$ the prefactor $A(\varphi_{2\mathrm{D}})$ for the relaxation rate in Eq. (2) can be compared to the analytic result, Eq. (11). The comparison in Fig. 4 for low to moderate packing fractions $\varphi_{2\mathrm{D}}$ corroborates that the theoretical prediction is in fact an exact result.

Conclusions.—We have demonstrated the emergence of a divergent time scale for the coupling of lateral to transverse degrees of freedom in a strongly confined fluid. The main insight has been that in collisions the momentum transfer becomes more and more planar as the wall separation is reduced. The dependence of the divergent time scale on the plate separation and packing fraction of the fluid has been worked out analytically including the prefactor by evaluating the dominant contribution of the collision operator and compared to our simulations. Remarkably, the theory is not limited to fluids but also applies to the ordered phase. We emphasize that the reference system is strongly interacting, and our calculation is one of the rare cases where analytic results can be elaborated.

The mechanism unraveled for the emergence of a slow time scale and the scaling with the transverse dimension should also hold for other geometries, such as liquids in narrow cylindrical tubes or quasi-1D confinement (see Supplemental Material [54]).

The hard-core interaction is of course an idealization of a short-ranged potential, but we anticipate our results to remain valid for the case of smooth potentials. More precisely, for hard spheres the collisions are instantaneous, whereas for smooth potentials the duration of a collision introduces a new time scale into the problem. As long as the Knudsen time scale L/v_{th}, i.e., the typical time for a particle to traverse the slit, is still much larger than the duration of a collision, the mechanisms for small transverse momentum transfer should be identical (see Supplemental Material for simulation results on smooth potentials [54]). Similarly, a smooth particle-wall interaction should not modify our findings, provided its range is much smaller than the slit width, and the transverse energy includes the wall potential in addition to the transverse kinetic energy.

It is also of interest to consider the opposite case where the duration of a collision is much longer than the time to traverse the slit. Then the use of a collision operator is no longer justified; rather, the collision events can be averaged over the fast transverse oscillations. Analytic progress in this direction has been made very recently [61], and it turns out that the predicted relaxation time for this case scales with a different power in the wall separation. Furthermore, the relaxation of the kinetic energy becomes exponential at times much longer than the Knudsen time, while for hard spheres it is exponential for all times.

The diverging relaxation time separates the decoupled two-dimensional dynamics from the coupled one in strong confinement. This should have drastic implications for systems in the vicinity of the glass transition such that the divergent structural relaxation time competes with the relaxation time of the coupling. In fact, the mode-coupling theory for confinement [47] suggests that the limits $t \to \infty$ and $L \to 0$ do not commute and different glassy dynamics on different time scales is expected.

The decoupling property of the transverse and lateral degrees of freedom in the equilibrium ensemble implies a divergent time scale for their dynamic coupling. The precise form of the divergence should depend on the microdynamics and should be different for the case of

Brownian dynamics, which can be realized experimentally for colloids confined between glass plates. Yet, to measure the divergent time scale in this case an observable needs to be chosen that does not relax quickly to equilibrium even without the close-to-planar collisions. An example could be the in-plane self-intermediate scattering function $F^s(q,t)$ at small wave numbers q, which probes the planar dynamics at large lateral length scales $2\pi/q$. Upon decreasing the wave number the relaxation time slows down as $\sim q^{-2}$ by diffusion and the crossover from purely 2D motion to the 3D confined coupled dynamics should be visible. A second, more challenging candidate for such an observable is the generalized intermediate scattering functions for fluids close to the glass transition.

We gratefully acknowledge many discussions with Rolf Schilling on our simulation results and on the emergence of the diverging time scale. This work has been supported by the Deutsche Forschungsgemeinschaft DFG via the Research Unit FOR1394 "Nonlinear Response to Probe Vitrification."

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