Dynamical properties of densely packed confined hard-sphere fluids

Gerhard Jung,¹,∗ Michele Caraglio,¹ Lukas Schrack,¹ and Thomas Franosch¹

¹Institut für Theoretische Physik, Universität Innsbruck, Technikerstraße 21A, A-6020 Innsbruck, Austria

Numerical solutions of the mode-coupling theory (MCT) equations for a hard-sphere fluid confined between two parallel hard walls are elaborated. The governing equations feature multiple parallel relaxation channels which significantly complicate their numerical integration. We investigate the intermediate scattering functions and the susceptibility spectra close to structural arrest and compare to an asymptotic analysis of the MCT equations. We corroborate that the data converge in the β-scaling regime to two asymptotic power laws, viz. the critical decay and the von Schweidler law. The numerical results reveal a non-monotonic dependence of the power-law exponents on the slab width and a non-trivial kink in the low-frequency susceptibility spectra. We also find qualitative agreement of these theoretical results to event-driven molecular-dynamics simulations of polycrystalline hard-sphere systems. In particular, the non-trivial dependence of the dynamical properties on the slab width is well reproduced.

I. INTRODUCTION

The structural relaxation of dense liquids displays a drastic slowing down of transport upon compression or cooling, a phenomenon commonly identified with the glass transition [1]. Upon approaching this transition, a supercooled bulk liquid exhibits several fascinating dynamical properties, in particular, the aforementioned slowing down, stretching of the intermediate scattering function, as well as a two-step power-law-relaxation behavior. All of these features have been observed in experiments [2–10] and simulations [11–18] and were successfully described by mode-coupling theory of the glass transition (MCT) [1, 19–22]. The underlying microscopic picture behind MCT is the trapping of particles in transient “cages” which are formed by their respective neighbors. Consequently, confining the supercooled liquid between two parallel walls is expected to have a significant impact on the nature of the glass transition [23–25]. Strong confinement will hinder or promote the formation of “cages” and the wall-particle interaction will induce layering [26, 27], thus drastically changing the local structure in the fluid. Analyzing the consequences of confinement is therefore of fundamental interest, not only to question the microscopic picture of the glass transition but also to better understand physical, chemical, and biological systems where confinement occurs naturally like porous rocks or crowded living cells.

In the last twenty years confined liquids have therefore been studied extensively in experiments [28–38] and simulations [27, 39–55], showing that even general questions like whether confinement accelerates or hinders the dynamics depends on the nature of the wall-particle potential [49, 51, 54] or the surface roughness [40, 44, 50]. Additionally, it has been found that confinement even with suppressed layering leads to significant changes in the static and dynamical properties of the liquid [39, 56–58].

To better understand supercooled liquids in confinement MCT was extended to describe a simple fluid confined between two parallel, flat and hard walls (cMCT) [24, 55, 59, 60]. The theoretical description depends on the introduction of symmetry-adapted fluctuating density modes which mirror the broken translational symmetry in lateral direction and lead to matrix-valued structure factors and intermediate scattering functions. The validity of this description for the statical properties and nonergodicity parameters of hard-sphere glasses has been investigated and confirmed by event-driven molecular dynamics simulations [55, 60]. A remarkable feature of cMCT is the emergence of a multiple reentrant glass transition for liquids with constant packing fraction in a slab of variable slit width [24, 59], which could also be observed using computer simulations [55, 60]. Interestingly, it also has been shown that the lines of constant chemical potential do not overlap with the glass-transition lines in a nonequilibrium state diagram, indicating that in a wedge geometry the observation of a coexistence between glass and liquid regions is anticipated.

A fundamental difference between the mathematical structure of the MCT equations in confined geometry to MCT in simple liquids is the emergence of multiple relaxation channels. These arise naturally due to a splitting of the particle-conservation law into distinct currents in lateral and transverse direction. Recently, it has been shown for MCT with multiple relaxation channels that under very mild assumptions the β-scaling equation is still valid despite this change of structure [61]. This allows us to perform a full asymptotic analysis of the dynamics by computing the power-law exponents for the critical decay and the von Schweidler law from microscopic expressions.

Here we focus on the dynamical properties of strongly confined liquids as encoded in MCT. For the first time we present a numerical solution for the full time dependence of the cMCT equations. We investigate the behavior of the dynamic correlation functions close to structural arrest and compare the results to glass-forming liquids in bulk. Additionally, we calculate the asymptotic power laws using the analysis presented in Ref. [61] and

*gerhard.jung@uibk.ac.at
show that they accurately describe the numerical solution in the $\beta$-scaling regime. We also investigate similarities and differences of our theoretical results and event-driven molecular dynamics simulations. The overall goal is to gain a better insight into the effects of confinement on supercooled liquids.

The manuscript is organized as follows: In Sec. II we recapitulate the mode-coupling theory in slit geometry and present the equations of motion for the intermediate scattering function. In order to enable a numerical integration we reformulate these equations by introducing an effective memory and apply an additional diagonal approximation. Afterwards, the numerical solution of the cMCT equations for the intermediate scattering function is presented in Sec. III and compared to the asymptotic analysis. In Sec. IV we then compare the dynamics predicted by cMCT to computer simulations. We summarize and conclude in Sec. V.

II. MODE-COUPLING THEORY IN SLAB GEOMETRY

A. Equations of motion

The fluctuating density modes of $N$ particles confined in a channel of accessible width $L$ can be introduced as [24],

$$\rho_\mu(q, t) = \sum_{n=1}^{N} \exp[iQ_\mu z_n(t)] e^{iq \cdot r_n(t)},$$

(1)

with particle positions $x_n = (r_n, z_n)$, restricted to the positions $-L/2 \leq z_n \leq L/2$, wave vectors $q = (q_x, q_y)$ and wavenumbers $Q_\mu = 2\pi \mu/L$. In the following, we will refer to the indices $\mu \in \mathbb{Z}$ as mode indices. The packing fraction is defined as $\nu = N\pi a^3/6V$, with particle diameter $a$, volume $V = AH$, wall area $A$ and wall distance $H = L + \sigma$. Directly connected to the fluctuating density modes is its coherent time-dependent correlation function,

$$S_{\mu\nu}(q, t) = \frac{1}{N} \langle \rho_\mu(q, t)^* \rho_\nu(q, 0) \rangle.$$  

(2)

Its initial value $S_{\mu\nu}(q) = S_{\mu\nu}(q, t = 0)$ is the structure factor, generalized to the slit geometry.

For this setting the Zwanzig-Mori projection operator formalism [1, 62, 63] with $\{\rho_\mu(q, t)\}$ as set of distinguished variables was applied [24, 59] to derive the equations of motion for the intermediate scattering functions $S_{\mu\nu}(q, t)$,

$$\dot{S}(t) + \int_0^t K(t-t')S^{-1}(t')dt' = 0.$$  

(3)

Here, we have dropped the explicit dependence on the (magnitude of the) wave vectors $q$ and introduced the matrix notation $[S(t)]_{\mu\nu} = S_{\mu\nu}(q, t)$. The memory kernel $K(t)$ describes the non-Markovian dynamics of the intermediate scattering function and is related to the dynamic correlation function of the density modes, $\dot{\rho}_\mu(q, t)$.

To derive an expression for the memory kernel, we consider the continuity equation for the density modes,

$$\dot{\rho}_\mu(q, t) = i \sum_{\alpha=\parallel,\perp} b^\alpha(q, Q_\mu) j^{\alpha\mu}(q, t),$$

(4)

with the selector $b^\alpha(x, z) = x\delta_{\alpha\parallel} + z\delta_{\alpha\perp}$ depending on the channel index $\alpha \in \{\parallel, \perp\}$, and the current channels $j^{\alpha\mu}(q, t)$. Since the currents in lateral ($\perp$) and longitudinal ($\parallel$) direction are anticipated to behave differently, the memory kernel $K(t)$ splits naturally into multiple decay channels,

$$K_{\mu\nu}(q, t) = [\mathcal{C}\{\mathcal{K}\}]_{\mu\nu} := \sum_{\alpha,\beta=\parallel,\perp} b^\alpha(q, Q_\mu) K^{\alpha\beta}_{\mu\nu}(q, t)b^\beta(q, Q_\nu).$$

(5)

By performing a second Zwanzig-Mori projection step using the current modes $\{j^{\alpha\mu}(q, t)\}$ as distinguished variables the equations of motion for the components of the memory kernel $K^{\alpha\beta}_{\mu\nu}(q, t)$ can be derived. This yields the result,

$$\mathcal{J}^{-1}K(t) + \mathcal{D}^{-1}K(t) + \int_0^t \mathcal{M}(t-t')K(t')dt' = 0,$$  

(6)

with the matrix notation $[\mathcal{K}(t)]^{\alpha\beta}_{\mu\nu} = K^{\alpha\beta}_{\mu\nu}(q, t)$ and

$$\mathcal{J}^{\alpha\beta}(q) = K^{\alpha\beta}_{\mu\nu}(q, t = 0) = v_{th}^2 n_\mu^* n_\nu \delta_{\alpha\beta}.$$  

(7)

Here, we have introduced the thermal velocity $v_{th} = \sqrt{k_B T/m}$ related to particle mass $m$ and the thermal energy $k_B T$, as well as the decomposition of the inhomogeneous density profile $n(z)$ into Fourier modes

$$n_\mu = \frac{1}{L/2} \int_{-L/2}^{L/2} n(z) \exp[iQ_\mu z] \, dz, \quad \mu \in \mathbb{Z}.$$  

(8)

We also included an instantaneous damping term given by a positive semidefinite Hermitian matrix in the mode and channel indices, $\mathcal{D}^{-1} \succeq 0$.

Mode-coupling theory now provides an approximation for the force kernel $\mathcal{M}(t)$ as a bilinear functional of the intermediate scattering functions $S_{\mu\nu}(q, t)$ [24, 59],

$$\mathcal{M}^{\alpha\beta}_{\mu\nu}(q, t) = \mathcal{F}^{\alpha\beta}_{\mu\nu}[S(t); q],$$

(9)

with

$$\mathcal{F}^{\alpha\beta}_{\mu\nu}[S(t); q] = \frac{1}{2N} \sum_{q_1 \in \mathbb{Q}_1} \sum_{\mu_1, \mu_2, \nu_1, \nu_2} \mathcal{Y}_{\mu_1\mu_2, \nu_1\nu_2}^{\alpha\beta}(q, q_1, q_2) S_{\mu_1\nu_1}(q_1, t) S_{\mu_2\nu_2}(q_2, t) \mathcal{Y}_{\nu_1\nu_2}^{\beta\alpha}(q, q_1, q_2)^*.$$  

(10)

where the vertices $\mathcal{Y}_{\mu_1\mu_2, \nu_1\nu_2}^{\alpha\beta}(q, q_1, q_2)$ are smooth functions of the control parameters,
oscillator equation with retarded friction

Here, the direct correlation function $c_{\mu}(q)$ is defined via the generalized Ornstein-Zernike equation [24, 59, 63, 64],

$$S^{-1} = \frac{n_{0}}{L^{2}} [v - c],$$

and the matrix $[v]_{\mu\nu} = v_{\mu - \nu}$, with $v(z) = n(z)^{-1}$ corresponds to the local volume. For given control parameters $S(q), c(q)$ and $n(z)$, the equations of motion, Eqs. (3), (6), and the mode-coupling functional $F^{\alpha\beta}_{\mu\nu}[S(t); q]$ define a closed set of integro-differential equations with unique solution $S(t)$ that also fulfills all the mathematical constraints of a correlation function [65].

Finding a numerical solution of the above equations of motion is, however, a non-trivial task. To stabilize the numerical schemes the introduction of an effective memory kernel $M(t)$ has been found to be very useful. To define $M(t)$ we employ the Laplace transformation,

$$LT \{ A(t) \} (z) = \hat{A}(z) := i \int_{0}^{\infty} A(t) e^{zt} dt,$$

and rewrite Eqs. (3) and (6),

$$\hat{S}(z) = -[zS^{-1} + S^{-1} \hat{K}(z)S^{-1}]^{-1},$$

$$\hat{K}(z) = -[zJ^{-1} + iD^{-1} + \hat{M}(z)]^{-1}.$$

This allows us to define the effective memory kernel $\hat{M}(z)$ implicitly via,

$$\hat{K}(z) = -[zJ^{-1} + iD^{-1} + \hat{M}(z)]^{-1},$$

where the effective matrices $J = C \{ J \}$ and $JD^{-1}J = C \{ JD^{-1}J \} \geq 0$ have been obtained by comparing the high-frequency behavior of the current kernel $K(z)$. In the time domain the equation of motion in terms of the effective memory kernel reduces to the standard harmonic oscillator equation with retarded friction

$$J^{-1} \dot{S}(t) + D^{-1}S(t) + S(t)S^{-1} + \int_{0}^{t} M(t - t') \dot{S}(t') dt' = 0.$$

**B. Diagonal approximation**

To solve Eq. (16) for the effective memory kernel, we rely on the diagonal approximation. We assume that off-diagonal terms can be discarded in the mode-coupling functional, $F^{\alpha\beta}_{\mu\nu}[S(t), q] = F^{\alpha\beta}_{\mu\nu}[S(t), q] \delta_{\alpha\beta} \delta_{\mu\nu}$, in the structure factor, $S_{\mu\nu}(q) = S_{\nu}(q) \delta_{\mu\nu}$, and the direct correlation function, $c_{\mu}(q) = c_{\nu}(q) \delta_{\mu\nu}$. Consistent with the Ornstein-Zernike equation, Eq. (12), we thus set $v_{\mu} = 0, \forall \mu \neq 0$ and $\mathcal{J}^{\alpha\beta}_{\mu\nu}(q) = \mathcal{J}^{\alpha\beta}_{\nu}(q) \delta_{\mu\nu} \delta_{\alpha\beta}$ with $\mathcal{J}^{\alpha\beta}_{\nu}(q) = v_{\nu}^{2}$. Furthermore, we assume that the instantaneous damping $D^{\alpha\beta}_{\mu\nu}(q) = \delta_{\alpha\beta} \delta_{\mu\nu} D_{\mu}(q)$ is also diagonal in mode and channel indices. As a consequence of the diagonal approximation the coupling of the intermediate scattering functions $S_{\mu}(q, t)$ for different wave numbers $q$ and mode indices $\mu$ arises purely on the level of the mode-coupling functional. It should be noted that the diagonal approximation is a technical approximation to obtain numerical results for the full time dependence which becomes exact in the planar and bulk limits [66]. It has been successfully applied to study the critical packing fraction and the non-ergodicity parameter for confined systems, where it has been compared to the solution without diagonal approximation [67] and to computer simulations [60, 68] with good agreement.

With this approximation, the left-hand side of Eq. (16) can be rewritten to find,

$$\frac{q^{2}}{zv_{\mu}^{2} + iD_{\mu}(q)z^{-1} + M_{\mu}(q, z)} + \frac{Q_{\mu}^{2}}{zJ_{\mu}(q)z^{-1} + iD_{\mu}(q)z^{-1} + M_{\mu}(q, z)} = 1,$$

which can be transformed into an integro-differential equation for the effective memory kernel in the time domain. For the sake of simplicity we will restrict ourselves to the case of $D_{\mu}(q) = D_{\mu}^{\perp}(q) = D_{0}$ and thus find,

$$\dot{M}_{\mu}(q, t) + v_{\mu}^{2}D_{0}^{-1}M_{\mu}(q, t) + M_{\mu}^{2}(q, t)dt' = v_{\mu}^{2}M_{\mu}(q, t) + \int_{0}^{t} \alpha_{\mu}(q, t - t')M_{\mu}(q, t')dt' + \int_{0}^{t} \beta_{\mu}(q, t - t')M_{\mu}(q, t')dt'.$$

Here, we have used that within the approximations introduced above

$$J_{\mu}(q) = (q^{2} + Q_{\mu}^{2})v_{\mu}^{2},$$

$$D_{\mu}(q) = (q^{2} + Q_{\mu}^{2})D_{0},$$

and abbreviated

$$\alpha_{\mu}(q, t) = J_{\mu}(q)^{-1}(Q_{\mu}^{2}M_{\mu}(t) + q^{2}M_{\mu}^{2}(t)),$$

$$\beta_{\mu}(q, t) = J_{\mu}(q)^{-2}(q^{2}M_{\mu}^{2}(t) + Q_{\mu}^{2}M_{\mu}(t)).$$

The initial value for the effective memory kernel is generally given by $J(t = 0)J = -JD^{-1}JD^{-1}J + C \{ JD^{-1}JD^{-1}J \} + C \{ JM(t = 0)J \}$. In our case this reduces to,

$$M_{\mu}(q, t = 0) = v_{\mu}^{2} \beta_{\mu}(q, t = 0).$$
III. NUMERICAL SOLUTION OF THE MCT EQUATIONS

In this section we investigate the intermediate scattering function (ISF) \( S_\mu(q,t) \) and the associated frequency-dependent dynamic susceptibility

\[
\chi''_\mu(q,\omega) := \omega \int_0^\infty S_\mu(q,t) \cos(\omega t) dt, \tag{25}
\]

within the diagonal approximation. The static input functions, namely the structure factor \( S_\mu(q) \), the direct correlation function \( c_\mu(q) \) and the density profile \( n(z) \) are calculated for monodisperse hard spheres using fundamental measure theory (FMT) and the Ornstein-Zernike equation with the Percus-Yevick closure, as described in Refs. [24, 57, 59]. The instantaneous damping terms are calculated for monodisperse hard spheres using fundamental measure theory (FMT) and the Ornstein-Zernike equation with the Percus-Yevick closure, as described in Refs. [24, 57, 59]. Appendix A provides details on the numerical discretization scheme which are important to achieve the desired numerical accuracy. For the numerical Fourier transform for the susceptibilities we rely on the modified Filon-Tuck algorithm [73, 74].

A. Dynamics close to the glass transition

We start the analysis for an accessible width \( L = 2.0\sigma \). The (normalized) intermediate scattering functions close to the glass transition is displayed in Fig. 1. As it is known from simple bulk liquids, the dynamics in the vicinity of the glass transition manifests itself within MCT via an algebraic decay to an extended plateau. In the liquid regime (\( \epsilon = (\varphi - \varphi_c)/\varphi_c < 0 \)) this plateau is followed by a structural relaxation on a time scale, that diverges as the critical packing fraction is approached. Importantly, for any fixed finite time \( t \), the intermediate scattering function \( S_\mu(q,t) \) varies smoothly with the packing fraction. Above the critical packing fraction \( (\epsilon > 0) \), the structure is not able to fully relax anymore and ergodicity breaking is observed, characterized by a non-zero value for the long-time limit, \( F_\mu(q) := S_\mu(q,t \to \infty) \). The two-step relaxation scenario in the supercooled regime can also be observed in the susceptibility spectrum (see Fig. 2). For frequencies much smaller than the microscopic ones, the susceptibilities display a power-law increase \( \propto \omega^a \) reflecting the critical decay towards the plateau in the time domain. On the liquid side a second power law \( \propto \omega^{-b} \) emerges at even lower frequencies corresponding to the von Schweidler law as the initial part of the terminal structural relaxation. Both power-law processes are connected by a pronounced minimum which is by orders of magnitude enhanced relative to a trivial superposition of Debye peaks. The low-frequency peak is known as \( \alpha \)-peak and appears stretched on the high-frequency flank whereas it behaves regularly at its low-frequency flank. A comparison of these spectra to the ones of simple bulk liquids [75] shows that in the case of comparatively large channel widths no qualitative differences are observed.

The situation is rather different for a channel width \( L = 1.0\sigma \) as shown in Fig. 3. While the two-step relaxation scenario is still observable there is a distinct kink in the high-frequency flank of the \( \alpha \)-peak of the dynamic susceptibility. A similar feature was recently observed in...
Ref. [61] for a Bosse-Krieger model with two decay channels. Concluding from this model, it seems natural that the reason for the emergence of the kink is an asymmetry of the two decay channels, parallel and perpendicular to the wall, since this asymmetry increases for decreasing wall separation. We will discuss this observation further in section III C.

In the following we analyze in detail the two relaxation processes: the critical decay and the von Schweidler law.

### B. β-scaling regime

The critical spectra shown in the last subsection indicate that the β-scaling regime exists also in case of strong confinement. This is not surprising since the asymptotic analysis for MCT with multiple relaxation channels in Ref. [61] showed the existence of a well defined β-scaling equation under very moderate assumptions, which are all fulfilled here (i.e. discontinuous transition in all modes). This enables us to perform an asymptotic analysis of the MCT equations in confinement similar to the one performed for simple bulk liquids [75]. For this we first determine the critical packing fraction \( \varphi_c \) using the standard iteration for the nonergodicity parameter \( F_\mu(q) \) (see e.g. Ref. [24]). Using Eq. (19) in Ref. [61] we can then determine the Frobenius-Perron eigenvector and thus Götze’s exponent parameter \( \lambda \) which encodes the critical exponents \( a \) and \( b \). The important quantities that were determined from the described analysis can be found in Table I.

The critical decay of the intermediate scattering function and the frequency-dependent susceptibility spectra are shown in Fig. 4 for different mode indices \( \mu \) and wave vectors \( q \). For times \( t \gtrsim 10^3 \sigma v^{-1}_h \) (frequencies \( \omega \lesssim 10^{-3} \nu_{th} \sigma^{-1} \)) there is no visible discrepancy between the asymptotic power laws and the numerical solution of the MCT equations. The decay from the plateau in the intermediate scattering function and the corresponding asymptotic power law for a packing fraction slightly below the critical value \( \varphi_c \) is then highlighted in Fig. 5 (upper panel). The lower panel demonstrates the validity of the von Schweidler law. In these figures no qualitative difference to the critical dynamics in bulk systems can be observed. It should, however, be emphasized that these results crucially depend on the correct fundamental constant \( \lambda \) which is different from the constant \( \lambda \) one would find without splitting of the relaxation channels such as in bulk liquids (see Table I and App. B). Depending on the dissimilarity of the two decay channels this can lead to significant corrections that need to be taken into account to match the numerical solution and the asymptotic power laws.

The most important discrepancy between bulk and confined liquids are the observed power-law exponents which significantly depend on the channel width. This quantitative impact of confinement on the asymptotic scaling laws will be analyzed in the next subsection.

### C. Effect of confinement

The effect of confinement on the nonequilibrium-state diagram has been studied in detail in Refs. [24, 55, 59, 60]. In these works a multiple reentrant glass transition was found which can also be observed in computer simulations [55, 60]. The reason for this behavior can be rationalized qualitatively with the competition of two length scales: the (average) particle diameter \( \bar{\sigma} \) and the wall separation \( H \). If the ratio of wall separation and average particle diameter \( n = H/\bar{\sigma} \) is an integer, \( n \in \mathbb{N} \), there are naturally \( n \) different layers in the system which enable a relatively large longitudinal diffusion. For half-integer \( n \), however, there are particles between the layers which significantly slows down the dynamics (incommensurate packing). This non-monotonic dependence on the channel width then becomes apparent in the structure factor, the critical packing fraction and the diffusion coefficient.
FIG. 4. Critical law highlighted in both the normalized coherent scattering function (upper panel) and the frequency-dependent susceptibility (lower panel) for accessible width \( L = 2.0\sigma \) and \( \varphi = \varphi_c \). Shown are different modes \( \mu \) and wavenumbers slightly below \((q_0\sigma = 3.42)\), directly at \((q_m\sigma = 6.52)\) and slightly above \((q_g\sigma = 9.63)\) the first maximum in the structure factor \( S_0(q,0) \). The asymptotes in the upper and lower panel correspond to Eqs. (B6) and (B7), respectively. The time scale \( t_0 = 0.028\sigma v_{th}^{-1} \) was determined by matching to the asymptotic solution of \( S_0(q_m, t) \). The parameters for the asymptotic analysis are summarized in Table I.

FIG. 5. Same as Fig. 4 for the normalized intermediate scattering function (upper panel) and frequency-dependent susceptibility (lower panel) in the \( \alpha \)-relaxation regime for accessible width \( L = 2.0\sigma \) and \( \varphi = \varphi_c - 10^{-7} \). The asymptotes in the upper and lower panel correspond to Eqs. (B9) and (B10), respectively. The parameters for the asymptotic analysis are summarized in Table I.

as was shown in Refs. [24, 55, 59, 60]. Here, we will study its impact on the critical power-law exponents.

The critical decay and the von Schweidler law (lower panel) for the frequency-dependent susceptibility for different accessible widths \( L \) are displayed in Fig. 6. The most apparent difference between the curves is the significantly different power-law exponent for \( L = 1.0\sigma \) (strong confinement). To investigate this in more detail, the exponents are plotted vs. accessible width in Fig. 7. Strikingly, similar to the static quantities, also this plot shows a non-monotonic behavior of the critical exponent \( a \) and the von Schweidler exponent \( b \) with wall separation. This means that moderate confinement \( L > 1.25\sigma \) reduces the stretching of the correlation functions relative to the bulk system (an unstretched exponential would correspond to \( b \to 1 \)) but a further decrease of the accessible width then leads to stronger stretching. This shows that the effect of confinement has indeed a non-trivial impact on all features of glass-forming liquids. Interestingly, the convergence of the exponents to the bulk limit for hard spheres is very slow. We explain this with the inhomogeneous density profiles, which significantly alter the glass transition and are strongly pronounced even for large channels \( L > 4.5\sigma \). Furthermore, the critical packing fraction of the glass transition increases significantly with \( L \) (from \( \varphi_c(L = 2.5\sigma) = 0.437 \) to \( \varphi_c(L = 4.5\sigma) = 0.469 \)) which additionally amplifies the layering.

We now come back to the “kink” observed in the low-
FIG. 6. Critical law (upper panel, $\varphi = \varphi_c$) and von Schweidler law (lower panel, $\varphi = \varphi_c - 10^{-7}$) for the frequency-dependent susceptibility for different accessible widths $L$. The parameters for the asymptotic analysis are summarized in Table I.

FIG. 7. Dependence of the critical exponents on the accessible width $L$. The exponents were determined from the asymptotic analysis as described in Ref. [61]. The arrows indicate the value of the exponents in the bulk limit for hard spheres (arrows pointing to the right [75]) and hard discs (arrows pointing to the left [77]).

Additionally, there is no

IV. COMPARISON TO EVENT-DRIVEN MOLECULAR DYNAMICS SIMULATIONS

Event-driven molecular dynamics (EDMD) simulations [79–81] enable the exact integration of equations of motion for particles with hard-sphere interactions. Here we compare our theoretical results to simulation results that we have extracted from Ref. [55]. There the authors collected data for polydisperse hard spheres in confined geometry as in the current set-up. The introduction of polydispersity is necessary to suppress crystallization. The full numerical solution of the MCT equations presented in this manuscript now allows us to directly compare theoretical and simulation results for the dynamical properties of confined hard-sphere glasses (see Fig. 9).

On the one hand, significant quantitative differences between theory and simulations are expected because the polydispersity significantly reduces the effect of layering in the system and the differences between commensurate and incommensurate packing. This can already be seen in the phase diagram of the polydisperse hard-sphere system (see Fig. 6 (a) in Ref. [60]) and thus also reduces the differences in the intermediate scattering functions for various accessible widths $L$. Additionally, there is no
ideal glass transition in simulation (and experiments) of hard spheres because eventually the structure will fully relax, as is already known from simple bulk liquids.

On the other hand, there are several features that are shared by theory and simulations. Most prominent is the fact that also in this case structural relaxation is slower for the system with $L = 1.3\bar{\sigma}$ than for $L = 1.0\bar{\sigma}$ despite the general trend that confinement slows down the dynamics. This leads to a clear order of the curves which is the same for both theory and simulations. Furthermore, both theory and simulations exhibit a pronounced two-step relaxation scenario that was discussed in detail in the previous section.

It is also noteworthy that the dependence of the von Schweidler exponent on accessible width $L$ as predicted by MCT is in slight contradiction with event-driven simulations. In Ref. [40, 55] simulation results indicated that stretching could be strongest for incommensurate packing, which contradicts the conclusion drawn for MCT in the last section. One possible reason for the discrepancy could be the different control-parameter distances $\epsilon = (\varphi - \varphi_c(L))/\varphi_c(L)$ since the simulations for different accessible width $L$ were all performed at constant packing fraction $\varphi$ while the results reported for the theory were determined for $\varphi_c(L)$ and thus $\epsilon = 0$. If $|\epsilon|$ becomes too large this will have an impact on the simulation results.

V. SUMMARY AND CONCLUSION

In this manuscript we have presented a numerical solution of the MCT equations of motion in slab geometry. This enabled us to perform a deep analysis of the dynamics of confined hard-sphere glasses. We have found that there are no qualitative differences between the $\beta$-scaling regime in systems with moderate confinement and bulk systems. Only for very small accessible width $L \lesssim 1.25\bar{\sigma}$ a clear feature of the parallel relaxation scenario induced by the confinement has been observed in the form of a kink in the low-frequency susceptibility spectrum.

Additionally, we have applied an asymptotic analysis for MCTs with multiple relaxation channels to investigate the effect of confinement on the two asymptotic power laws: the critical decay and the von Schweidler law. We have observed that, similar to the non-monotonic dependence of the critical packing fraction, also the power-law exponents depend non-trivially on the channel width. For moderate confinement we have found

![FIG. 8. Normalized intermediate scattering function (upper panel) and frequency-dependent susceptibility (lower panel) in the $\alpha$-relaxation regime for channel width $L = 1.0\bar{\sigma}$. Shown are different modes $\mu$ and wave vectors slightly below $(q\sigma = 3.42)$, directly at $(q_m\sigma = 6.52)$ and slight above $(q_g\sigma = 9.63)$ the first maximum in the structure factor $S_0(q)$. The parameters for the asymptotic analysis are summarized in Table 1.](image1)

![FIG. 9. Comparison of MCT results for the coherent scattering function at volume fraction $\varphi = 0.42$ with event-driven molecular dynamics (EDMD) simulations at $\varphi = 0.52$. Simulation data are extracted from Ref. [55]. The simulations use a polydisperse mixture ($s = 15\%$) and $\bar{\sigma}$ denotes the average particle diameter.](image2)
that the stretching of the intermediate scattering function is decreased (corresponding to an increase of the von Schweidler exponent) while it is significantly increased for strong confinement, indicating stronger heterogeneous dynamics in the slit. Importantly, mode-coupling theory also predicts a very slow convergence of the critical exponents to the bulk limit for hard spheres.

The numerical results have also been compared to event-driven molecular dynamics simulations of confined, polydisperse hard spheres. Both theory and simulations exhibit a clear non-monotonic dependence of their dynamic properties on the channel width. Yet, a comparison beyond identifying the relevant trends is unfeasible due to the different polydispersities and the known discrepancies of the ideal transition as predicted by MCT to the dynamic crossover in simulations and experiments.

This work opens up the possibility of a throughout analysis of various aspects of confined fluids with mode-coupling theory. Possible future projects are the incorporation of Brownian dynamics [82] and the study of single particle properties like self-intermediate scattering functions [83] or mean-square displacements. Importantly, the latter would enable a significantly better comparison with computer simulations. This can for example facilitate the search for a similar kink as observed in the MCT solution of the low-frequency susceptibility spectrum. Additionally, it will be interesting to look for signatures of parallel relaxation in experimental measurements of dielectric spectra of molecules or confined particles. Furthermore, using static quantities from computer simulations for extreme confinement could enable the cMCT analysis of the dimensional crossover to the planar bulk limit for hard discs [84, 85]. Currently this is not possible since the iterative techniques to determine the static input functions do not converge in extreme confinement.

ACKNOWLEDGMENTS

We gratefully acknowledge inspiring discussions with Suvendu Mandal. We thank Matthias Sperl for drawing our attention to the Cole-Cole peak. This work has been supported by the Austrian Science Fund (FWF): I 2887.

Appendix A: Details on the numerical discretization scheme

The correlation functions appearing in this manuscript depend on a mode index, a wavevector and time. In the following, we will describe how these dependences are handled to obtain a numerical integration scheme for the MCT equations of motion. The parameters used in this manuscript are summarized in Table II.

| $d_2/\sigma$ | $d_2/\sigma$ | MCT |
|-------------|-------------|-----|
| 30          | 5           |     |

TABLE II. Summary of the parameters used for creating the static input using fundamental measure theory (FMT) and the Ornstein-Zernike equation with the Percus-Yevick closure (OZ+PY) as well as the numerical integration of the mode-coupling equations of motion (17) and (19).

The parameters $d_2$ and $n_z$ were used for the spatial linear discretization. The approximate excess free energy functional used is the White-Bear mark II (WBII) functional [86, 87]. The parameters $D_1$ and $D_2$ were used for the spatial linear discretization in $z$-direction with $n_z = L/d_2$. The $r$-direction is logarithmically discretized in the range $[r_{\min}, r_{\max}]$ with $N_r$ grid points. Details in Refs. [57, 67].

1. Mode index

The mode index is already discrete due to the finite channel width. However, for the numerical solution we have to introduce a cutoff $|\mu| \leq M$, chosen such that the neglected orders do not have a significant impact on the main modes anymore. Empirically we found $M = 5$ to be a reasonable cutoff for $L \lesssim 2r$. For the results in Fig. 7 we use $M = 10$ for $L \lesssim 3.5\sigma$ and $M = 15$ otherwise.

2. Wavevector

As done in Ref. [24] we first introduce the thermodynamic limit of Eq. (10) by replacing,

$$\lim_{N,A \to \infty} \frac{1}{N} \sum_{\mathbf{q}_2 = \mathbf{q} - \mathbf{q}_1} \langle ... \rangle = \frac{1}{n_0(2\pi)^2} \int_0^\infty dq_1 \int_{|q - q_1|}^{q + q_1} dq_2 \frac{4q_1q_2}{\sqrt{4q_1^2q_2^2 - (q^2 + q_1^2 - q_2^2)^2}} \langle ... \rangle. \quad (A1)$$

Here, $A$ is the surface area of the box with volume $V = HA$. The $q$-dependence is then discretized to $q = q_0 + m\Delta q$, with $m = 0, ..., N_q - 1$. The integral is evaluated using a modified trapezoidal rule in which the value of the function to be integrated is not taken in the middle of two grid points, $q_m = m\Delta q$ and $q_{m+1}$, but at $q_m + q_0$, with $q_0 = 0.303\Delta q$. This provides the best discrete description of the Jacobian of the transformation to bipolar coordinates which allows to write the right term in Eq. (A1) [72, 88]. In this work we chose $N_q = 30$ and $\Delta q\sigma = 1.0345$ such that $q_{\max}\sigma = 30$. This choice
allows us the solve the equations of motion with the necessary accuracy in the dynamical correlation functions while the numerical error due to the \( q \)-discretization remains small.

3. Time

To find a numerical solution of the integro-differential equations, Eqs. (17) and (19), we need to discretize their time dependence such that the derived integration schemes are stable for about 15-20 orders of magnitude in time. To achieve this goal, we apply similar schemes as previously proposed in the MCT literature, like decimation \([61, 69, 71]\), which shall not be repeated here. In the following, we will list some important remarks that are necessary to stabilize the numerical discretization scheme.

- As discussed in Ref. [61], Appendix B, we find that taking the time derivative on both sides of Eq. (19) and discretize the obtained second order integro-differential equation yields a significantly more stable numerical scheme for longer times. Starting from decimation step \( D_1 \) we therefore integrated the memory kernel with this second-order equation which has the same form as Eq. (17). The applied discretization scheme is thus the same as for the integration of the scattering function.

- We symmetrize the discretized convolution integrals in the same way as described in Ref. [61], Appendix B.

- The instantaneous contributions to the memory kernels, \( D^{-1} \) and \( D^{-1} \), are explicitly included to the values of \( M(t = 0) \) and \( \mathcal{M}(t = 0) \), respectively. We thus obtain,

\[
\dot{M}_\mu(q, t = 0) = \beta_\mu(q, t = 0) + D_\mu(q)^{-1} \Delta t, \quad (A2)
\]

\[
\dot{\mathcal{M}}_{\mu}^\parallel(q, t = 0) = \mathcal{F}_\mu^\parallel |S(t = 0); q| + D_0^{-1} \Delta t. \quad (A3)
\]

This yields a more compact numerical integrator. The integration scheme using moments (see Refs. [69, 71]) ensures that these contributions are handled correctly in the decimation steps.

Taking all this into account we arrive at the following integration scheme for the coherent scattering function (not including the explicit dependence on \( q \) and \( \mu \)),

\[
A_{S} S_i = 2.5 S_{i-1} - 2 S_{i-2} + 0.5 S_{i-3} \\
+ \frac{\Delta^2 J}{4} \left( 2 d \tilde{M}_1 S_{i-1} + 2 \tilde{M}_0 - \tilde{M}_{i-2} S_i - \tilde{M}_i S_{i-1} \right) \\
- \frac{\Delta^2 J}{2} \sum_{j=1}^{i} d S_j (\tilde{M}_{i-j+1} - \tilde{M}_{i-j}) \\
- \frac{\Delta^2 J}{2} \sum_{j=2}^{i} d \tilde{M}_j (S_{i-j+1} - S_{i-j}) \\
- \frac{\Delta^2 J}{4} \left( d S_{i-1} (\tilde{M}_{i+1} - \tilde{M}_i) \right. \text{ if } i \neq i - \bar{i} \\\n\left. + 0 \right \text{ otherwise} \\
- \frac{\Delta^2 J}{4} \left( d \tilde{M}_{i-1} (S_{i+1} - S_i) \right. \text{ if } i \neq i - \bar{i} \\\n\left. + 0 \right \text{ otherwise}, \\
A_S = 1 + \frac{\Delta^2 J}{2} \left( S_{i-1}^{-1} + d \tilde{M}_1 \right), \quad (A4)
\]

with \( S_i = S(i \Delta t) \), \( d S_i = \Delta t^{-1} \int_0^{\Delta t} d t' S(t') \) and similarly \( M_i, d M_i \). We also introduced \( i = [i/2] \). The brackets \( [j] \) denote the largest integer less or equal \( j \). Before decimation step \( D_1 \) the effective memory kernel is integrated via,

\[
A_{M_i} M_i = 4/3 M_{i-1} - 1/3 M_{i-2} - \frac{\Delta^2 v_{th}^4}{3} \alpha(d M_1) M_{i-1} \\
+ v_{th}^4 (\beta[M] - 4/3 \beta[M_{i-1}] + 1/3 \beta[M_{i-2}]) \\
- \frac{\Delta^2 v_{th}^4}{3} \sum_{j=1}^{i-1} \alpha [M_{i-j+1} + \alpha[M_{i-j}]] \\
- \frac{\Delta^2 v_{th}^4}{3} \sum_{j=2}^{i-1} \alpha [M_{i-j+1} + \alpha[M_{i-j}]] \\
+ \frac{\Delta^2 v_{th}^4 J_i^{-1}}{3} \sum_{j=1}^{i-1} \alpha [M_{i-j+1} + \alpha[M_{i-j}]] \\
+ \frac{\Delta^2 v_{th}^4 J_i^{-1}}{3} \sum_{j=1}^{i-1} \alpha [M_{i-j+1} + \alpha[M_{i-j}]] \\
A_{M_1} = 1 + \frac{\Delta^2 v_{th}^4}{3} \alpha(d M_1), \quad (A5)
\]

where we defined \( \alpha[B] = J_{\mu}(q)^{-1}(Q_{\mu}^{2} B_{\mu}^{2}(t) + q^{2} B_{\mu}^{2}(t)) \) and \( \beta[B] = J_{\mu}(q)^{-2}(q^{2} B_{\mu}^{2}(t) + Q_{\mu}^{2} B_{\mu}^{2}(t)) \). As discussed before, after decimation step \( D_1 \) we change the integra-
tion algorithm and use,

\[ A\mathcal{M}_i \mathcal{M}_j = 2.5 M_{i-1} - 2 M_{i-2} + 0.5 M_{i-2} \]
\[ + \frac{\Delta t^2 v_{th}^4}{4} (2\alpha[d\mathcal{M}_1] M_{i-1} - \alpha[M_{i-1}] M_i - \alpha[M_j] M_{i-j}) \]
\[ + v_{th}^4 (\beta[M_i] - 2.5 \beta[M_{i-1}] + 2 \beta[M_{i-2}] - 0.5 \beta[M_{i-3}]) \]
\[ - \frac{\Delta t^2 v_{th}^4}{2} \sum_{j=1}^{i} \alpha[d\mathcal{M}_j] (M_{i-j+1} - M_{i-j}) \]
\[ - \frac{\Delta t^2 v_{th}^4}{2} \sum_{j=1}^{i} \alpha[M_{i-j+1} - M_{i-j}] \]
\[ - \frac{\Delta t^2 v_{th}^4}{4} \left\{ \begin{array}{ll}
\alpha[d\mathcal{M}_{i-1}] (M_{i-1} - M_i) & \text{if } \tilde{i} \neq i - \tilde{i} \\
0 & \text{otherwise}
\end{array} \right. \]
\[ + \frac{\Delta t^2 v_{th}^4}{4} \left\{ \begin{array}{ll}
\alpha[M_{i-1}] (M_{i-1} - M_i) & \text{if } \tilde{i} \neq i - \tilde{i} \\
0 & \text{otherwise}
\end{array} \right. \]
\[ + \frac{\Delta t^2 v_{th}^4}{2} \sum_{j=1}^{i} \alpha[d\mathcal{M}_j] (M_{i-j+1} - M_{i-j}) \]
\[ + \frac{\Delta t^2 v_{th}^4}{2} \sum_{j=1}^{i} \alpha[M_{i-j+1} - M_{i-j}] \]
\[ + \frac{\Delta t^2 v_{th}^4}{4} \left\{ \begin{array}{ll}
\alpha[d\mathcal{M}_{i-1}] (M_{i-1}^+ - M_i^+) & \text{if } \tilde{i} \neq i - \tilde{i} \\
0 & \text{otherwise}
\end{array} \right. \]
\[ + \frac{\Delta t^2 v_{th}^4}{4} \left\{ \begin{array}{ll}
\alpha[M_{i-1}] (M_{i-1}^+ - M_i^+) & \text{if } \tilde{i} \neq i - \tilde{i} \\
0 & \text{otherwise}
\end{array} \right. \]
\[ \mathcal{M}_{th} = 1 + \frac{\Delta t^2 v_{th}^4}{2} \alpha[d\mathcal{M}_1]. \]  

(A6)

In each time step, \( S_i \) is initialized by setting \( S_i = S_{i-1} \). With this the memory kernels \( \mathcal{M}_m^a(q) \) are calculated using Eq. (10) in the thermodynamic limit as described in Eq. (A1). \( S_i \) is then determined self-consistently by solving Eqs. (A4) and (A5)/(A6) until the convergence reaches an accuracy of \( \max_{q,\mu} |S_n^{a}(q) - S_{n-1}(q)| < \epsilon_a \) in the \( n \)-th iteration step as described in Refs. [69, 89].

Appendix B: Asymptotic expansion

In Ref. [61] an asymptotic analysis of mode-coupling theory equations with multiple relaxation channels has been presented. The reference proves the validity of the \( \beta \)-scaling equation and derives relations for the critical exponents that characterize the slowing down at the glass transition. In the following, we recapitulate the most important relations and describe how they can be applied to the mode-coupling equation in confined geometry.

Starting from the equations for structural relaxation, Eqs. (14) and (15), with negligible contributions of \( z\mathcal{F} + i\mathcal{D}^{-1} \), we perform an asymptotic expansion using the ansatz \( S(q,t) - F_c(q) = \sqrt{\sigma} \mathcal{G}^{(1)}(t) + \mathcal{O}(\sigma) \), for a small separation parameter \( \sigma \). (In this appendix, we follow the standard MCT notation and \( \sigma \) denotes a separation parameter, not the hard-sphere diameter.) We thus assume that the correlator is close to its plateau value (i.e. the critical non-ergodicity parameter \( F_c(q) \)). It has been shown that close to the glass transition, \( \sigma = C \epsilon \), with constant \( C \) and control parameter \( \epsilon = (\varphi - \varphi_c)/\varphi_c \).

To first order we find the factorization theorem,

\[ \mathcal{G}^{(1)}(q,t) = \mathcal{H}(q) g(\hat{t} = t/t_o), \]  

(B1)

stating that close to the glass transition on a time scale \( t_o \) all dynamical correlation functions can be rescaled by the critical amplitudes \( \mathcal{H}(q) \) to superimpose on a single universal master curve \( g(\hat{t}) \).

The equation of motion for this master curve is then derived as solubility condition by considering the second order of the expansion [61],

\[ \frac{d}{dt}(g * g)(\hat{t}) = \lambda g(\hat{t})^2 + \text{sgn} \sigma, \]  

(B2)

which is the well-known \( \beta \)-scaling equation. The exponent parameter \( \lambda \) connects the power law exponents for the critical decay, \( a \), and the von-Schweidler law, \( b \), via Götze’s exponent relation,

\[ \Gamma(1+b) = \lambda = \Gamma(1-a)/\Gamma(1-2a). \]  

(B3)

The subtleties derived in Ref. [61] are that this \( \beta \)-scaling equation is only found via rescaling, which is possible due to its scale invariance. From the asymptotic analysis we obtain,

\[ \lambda = \hat{\lambda}/(1-\Delta), \]  

(B4)

with channel asymmetry \( \Delta = 0 \) in case of bulk geometry. The parameters \( \mathcal{H}(q), C, \Delta \) and \( \hat{\lambda} \) are complicated functions of the mode-coupling functional in confined geometry (and therefore also the static input functions) as well as the critical non-ergodicity parameters (see Ref. [61] for details).

The workflow to apply the asymptotic expansion is the following:

- Find the critical packing fraction \( \varphi_c \) using binary search based on the asymptotic equation,

\[ S(q) - F(q) = [S(q)^{-1} + N(q)^{-1}], \]  

(B5)

where \( N(q) = C \left\{ \mathcal{F}[F(q); q]^{-1} \right\}^{-1} \). This equation can be readily used as self-consistent iteration scheme to determine the non-ergodicity parameter [24, 59] and such the ideal glass transition.

- Evaluate the critical non-ergodicity parameter, \( F_c(q) \), to calculate the mode-coupling functional at the critical point and thus the critical amplitude (using the eigenvalue equations (27)-(29) in Ref. [61]).
• Calculate the parameters $\tilde{\lambda}$ and $\Delta$ using Eqs. (38) and (39) in Ref. [61]. From this determine the power law exponents $a$ and $b$ with Eqs. (B4) and (B3).

• For $\epsilon \neq 0$, we can also directly calculate $\sigma$ using the non-ergodicity parameter $F_c(q)$ for $\varphi = \varphi_c(1 + \epsilon)$ (see Eq. (37) in Ref. [61]).

It is important to note that $\Delta \approx 0$ and thus $\tilde{\lambda} \approx \lambda$ implies that the relaxation channels parallel and perpendicular to the walls become very similar. It does, however, not mean that confinement has no influence on the full mode-coupling functional for confined geometry.

The asymptotic dynamics of the correlation functions can be directly extracted from the $\beta$-scaling equation, similar to bulk liquids (see Refs. [1, 75]). To summarize:

• For times $t$ much larger than the microscopic ones and $t \ll t_\sigma$ the short-time solution $g(t \ll 1) = t^{-a}$ sets $t_\sigma = t_0 |\sigma|^{-1/2a}$ and we obtain,

$$S(q, t) \simeq F_c(q) + H(q)(t/t_\sigma)^{-a} \sqrt{|\sigma|},$$  \hspace{1cm} (B6)

$$\chi''(q, \omega) \simeq H(q)T(1 - a) \sin (\pi a/2)(\omega t_\sigma)^a \sqrt{|\sigma|}.$$  \hspace{1cm} (B7)

Here, $\chi''(q, \omega) = \omega S''(q, \omega)$ is the dynamic susceptibility, determined from the Fourier cosine transform of the correlation function, $S''(q, \omega) = \int_0^\infty \cos(\omega t)S(q, t)dt$.

• For $\sigma > 0$ and $t \gg t_\sigma$ the non-ergodicity parameter is given by,

$$F(q) = \lim_{t \to \infty} S(q, t) \simeq F_c(q) + H(q)\sqrt{\sigma \Gamma(1 - \lambda)},$$  \hspace{1cm} (B8)

• For $\sigma < 0$ and $t \gg t_\sigma$ a second power law emerges, $g(t \gg 1) = -B^b t^\gamma$, corresponding to the early $\alpha$-relaxation on a time scale $t_\sigma = (t_0/B^{1/b}) |\sigma|^{-\gamma}$, with $\gamma = 1/2a + 1/2b$. For the correlation function and the dynamic susceptibility we find,

$$S(q, t) \simeq F_c(q) - H(q)(t/t_\sigma)^b,$$  \hspace{1cm} (B9)

$$\chi''(q, \omega) \simeq H(q)\Gamma(1 + b) \sin (\pi b/2)(\omega t_\sigma)^{-b}.$$  \hspace{1cm} (B10)

[1] W. Götze, Complex Dynamics of Glass-Forming Liquids - A Mode-Coupling Theory (Oxford University Press, Oxford, 2009).
[2] W. van Megen and S. M. Underwood, Phys. Rev. Lett. 70, 2766 (1993).
[3] W. van Megen and S. M. Underwood, Phys. Rev. E 49, 4206 (1994).
[4] G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, Phys. Rev. A 45, 3867 (1992).
[5] G. Li, W. M. Du, A. Sakai, and H. Z. Cummins, Phys. Rev. A 46, 3343 (1992).
[6] T. Franosch, M. Fuchs, W. Götze, M. R. Mayr, and A. P. Singh, Phys. Rev. E 56, 5659 (1997).
[7] A. Singh, G. Li, W. Götze, M. Fuchs, T. Franosch, and H. Cummins, J. Non-Cryst. Solids 235-237, 66 (1998).
[8] P. Lunkenheimer, A. Pimenov, M. Dressel, Y. G. Goncharov, R. Bömer, and A. Loidl, Phys. Rev. Lett. 77, 318 (1996).
[9] U. Schneider, P. Lunkenheimer, R. Brand, and A. Loidl, Phys. Rev. E 59, 6924 (1999).
[10] W. Götze and Th. Voigtmann, Phys. Rev. E 61, 4133 (2000).
[11] W. Kob and H. C. Andersen, Phys. Rev. Lett. 73, 1376 (1994).
[12] S. K. Das, J. Horbach, and Th. Voigtmann, Phys. Rev. B 78, 064208 (2008).
[13] P. Gallo, F. Sciortino, P. Tartaglia, and S.-H. Chen, Phys. Rev. Lett. 76, 2730 (1996).
[14] F. Sciortino, P. Gallo, P. Tartaglia, and S. H. Chen, Phys. Rev. E 54, 6331 (1996).
[15] F. Sciortino, L. Fabbian, S.-H. Chen, and P. Tartaglia, Phys. Rev. E 56, 5397 (1997).
[16] F. Sciortino and W. Kob, Phys. Rev. Lett. 86, 648 (2001).
[17] J. Horbach, W. Kob, and K. Binder, Philos. Mag. B 77, 297 (1998).
[18] Th. Voigtmann and J. Horbach, EPL 74, 459 (2006).
[19] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C: Solid State Phys. 17, 5915 (1984).
[20] W. Götze and L. Sjögren, Rep. Prog. Phys. 55, 241 (1992).
[21] W. Götze, J. Phys. Condens. Matter 11, A1 (1999).
[22] L. M. C. Janssen, Frontiers in Physics 6, 97 (2018).
[23] C. Alba-Siminesco, B. Coasne, G. Dosseh, G. Dudziak, K. E. Gubbins, R. Radhakrishnan, and M. Slivinska-Bartkowiak, J. Phys. Condens. Matter 18, R15 (2006).
[24] S. Lang, V. Botan, M. Oettel, D. Hajnai, T. Franosch, and R. Schilling, Phys. Rev. Lett. 105, 125701 (2010).
[25] F. Varnik and T. Franosch, J. Phys. Condens. Matter 28, 133001 (2016).
[26] Z. T. Németh and H. Löwen, Phys. Rev. E 59, 6824 (1999).
[27] J. Mittal, T. M. Truskett, J. R. Errington, and G. Hummer, Phys. Rev. Lett. 100, 145901 (2008).
[28] P. S. Sarangapani, A. B. Schofield, and Y. Zhu, Soft Matter 8, 814 (2012).
[29] P. S. Sarangapani, A. B. Schofield, and Y. Zhu, Phys. Rev. E 83, 030502(R) (2011).
[30] C. R. Nugent, K. V. Edmond, H. N. Patel, and E. R. Weeks, Phys. Rev. Lett. 99, 025702 (2007).
[31] G. L. Hunter, K. V. Edmond, and E. R. Weeks, Phys. Rev. Lett. 112, 218302 (2014).
[32] I. Williams, E. C. Oğuuz, P. Bartlett, H. Löwen, and C. Patrick Royall, J. Chem. Phys. 142, 024505 (2015).
[33] K. Nygård, R. Kjellander, S. Sarman, S. Chodankar,
