Friction in liquids arises from conservative forces between molecules and atoms. Although the hydrodynamics at the nanoscale is subject of intense research and despite the enormous interest in the non-Markovian dynamics of single molecules and solutes, the onset of friction from the atomistic scale so far could not be demonstrated. Here, we fill this gap based on frequency-resolved friction data from high-precision simulations of three prototypical liquids, including water. Combining with theory, we show that friction in liquids emerges abruptly at a characteristic frequency, beyond which viscous liquids appear as non-dissipative, elastic solids. Concomitantly, the molecules experience Brownian forces that display persistent correlations. A critical test of the generalised Stokes–Einstein relation, mapping the friction of single molecules to the visco-elastic response of the macroscopic sample, disproves the relation for Newtonian fluids, but substantiates it exemplarily for water and a moderately supercooled liquid. The employed approach is suitable to yield insights into vitrification mechanisms and the intriguing mechanical properties of soft materials.
Molecular friction is a key ingredient for dynamic processes in fluids: it limits diffusion, governs dissipation, and enables the relaxation towards equilibrium. In a liquid environment, the friction experienced by solvated molecules and nanoprobes exhibits a delayed response to external stimuli, indicating non-Markovian dynamics. Such memory is found on sub-picosecond up to microsecond scales; it has repercussions on macromolecular transition rates but is manifest in the visco-elastic behaviour of soft materials. However, the origin of friction from conservative forces between molecules and atoms remains as one of the grand challenges of the physics of fluids.

Stokes’ friction law, describing the resistance to a steadily dragged immersed sphere of radius $a$, links the friction $\zeta$ to the (macroscopic) shear viscosity $\eta_m$, and the relation $\zeta = 6\pi\eta_m a$ scales down remarkably well to single molecules. Stokes’ hydrodynamic treatment was actually more general and addressed slow oscillatory motions in viscous fluids, motivated by inaccuracies of pendulum clocks caused by air drag. These predictions of a dynamic friction $\zeta(\omega)$ that depends on the oscillation frequency $\omega$ have been interpreted in terms of a delayed response, also referred to as hydrodynamic memory, and have only recently been shown to be quantitative also for micron-sized particles. In the domain of micro-rheology, measurements of $\zeta(\omega)$ are used to infer the mechanical properties of complex fluids.

From the perspective of individual molecules or atoms, fluids are governed by conservative interactions and obey Newton’s equations of motion, yielding smooth and time-reversible trajectories. In particular, a single molecule is not subject to friction in this picture, and the mechanism of the required entropy production is far from obvious. Macroscopic friction and other transport coefficients have been linked to microscopic chaos and the Lyapunov spectrum of the liquid, but the connection of the latter to the corresponding Green–Kubo integrands, or equivalently, to the dynamic friction $\zeta(\omega)$, is an open issue. First-principle theories to friction are hampered by the fact that liquids are strongly interacting systems. An insightful, formal relation between the many-particle Liouville operator and dissipation spectra was derived in the seminal works by Zwanzig, Mori, and others, but the analytic evaluation of the resulting expressions hinges on uncontrolled approximations. For example, a systematic short-time expansion of the motion at all orders would yield zero friction (see “Methods”). Early work on dissipation spectra recognised the importance of exact sum rules, but the proposed ad hoc models, however, violate the sum rules at higher orders. Theoretical progress was made for hard-sphere fluids, where billiard-like collisions generate an instantaneous, Markovian contribution to friction, thereby rendering the frictionless regime inaccessible.

To gradually bridge between the atomistic and hydrodynamic regimes, one would ideally like to have a magnifying glass that allows for zooming from the slowest to the fastest processes, thus obtaining an increasingly sharper view of the molecular details. Spectral quantities such as $\zeta(\omega)$ can serve this purpose with the frequency $\omega$ as the control knob. Implementing this idea in simulations of liquids and numerically tracing the friction of molecules over wide frequency windows from fully developed dissipation all the way down to the non-dissipative regime would reveal sizable variations of $\zeta(\omega)$. Such deviations of $\zeta(\omega)$ from a constant friction $\zeta_0$ signify non-Markovian motion that is widely cast in the generalised Langevin equation. For three distinct liquids—water, a dense Lennard-Jones (LJ) fluid representing a simple, mono-atomic liquid, and a supercooled binary mixture serving as a model glass former—we obtained low-noise, cross-validated data for the dynamic friction $\zeta(\omega)$ and the frequency-dependent viscosity $\eta(\omega)$ over windows that span from the fastest to the slowest processes in each liquid. Corroborated by these data, we give rigorous arguments that dissipative processes in molecular liquids are exponentially fast suppressed as frequency is increased. As a consequence, the liquid’s response is purely elastic above a characteristic frequency $\omega_c$, a feature that goes beyond popular models of friction and viscoelasticity. Furthermore, the magnitude of friction cannot be inferred from the instantaneous behaviour of molecular trajectories: its origin is non-local in time. Finally, having data available for both $\zeta(\omega)$ and $\eta(\omega)$, we tested the connection between microscopic friction and the macroscopic mechanical properties of complex fluids, postulated by the generalised Stokes–Einstein relation:

$$\zeta(\omega) = \frac{\pi M^2 \omega^2}{4 \eta(\omega) a^2}.$$

Fig. 1 Dynamic friction bridges between the hydrodynamic and atomistic pictures of liquids. a A pendulum that oscillates in a viscous fluid with frequency $\omega$ experiences a dynamic friction $\zeta(\omega)$ as calculated by Stokes (1851) for slow motion. The associated flow pattern (stream lines) leads to a hydrodynamic memory of the motion. Magnifying the microscopic scale, the fluid consists of molecules that obey Newton’s equations, which are non-dissipative and generate smooth trajectories. Stokes’s result for the pendulum scales down to single molecules, and the function $\zeta(\omega)$ provides the bridge between the frictionless (microscopic) and the hydrodynamic (macroscopic) descriptions. b, c In liquids, the short-time trajectories of molecules (b) are smooth, but chaotic curves due to molecules rattling in transient cages formed by their neighbours (c brown spheres). The onset of friction is driven by the momentum transfer to the cage, as supported by control simulations of a single particle (red sphere) in a matrix of pinned particles (brown and yellow). Illustration for a mono-atomic fluid in two dimensions.
relation. The latter is found to either fail completely (mono-atomic liquid), serve as a qualitative description (water), or being a nearly quantitative relation (supercooled liquid).

Results

Molecular friction in liquids emerges rapidly. Instead of observing the response to an oscillatory force, we recorded the Brownian position fluctuations in equilibrium and link them to the friction, taking advantage of a fluctuation–dissipation relation. For the three liquids under investigation, we carried out molecular dynamics simulations to compute the mean-square displacement (MSD). Using the MSD as sole input, we estimated both the dynamic friction \( \zeta(\omega) \) and the memory function \( \gamma(t) \) in an ansatz-free approach, following two complementary routes that allow for cross-validation (see Fig. 2 and “Methods”). The first route invokes complex analysis and is based on the Fourier–Laplace transform of correlation functions, sampled on a sparse time grid (“adapted Filon algorithm”). Second and independently, we computed the antiderivative of \( \gamma(t) \) using a stable deconvolution technique for uniform time grids.

Although all three liquids display rather different dynamics, leaving distinct fingerprints in their friction spectra, their high-frequency behaviours of \( \zeta(\omega) \) share significant similarities (Fig. 3a–c). Most remarkably, the data demonstrate that beyond a liquid-characteristic frequency, \( \omega \gtrsim \omega_c \), the friction \( \zeta(\omega) \) goes exponentially fast to zero. Such a rapid spectral variation has to be contrasted to the typical algebraic peaks, i.e., the Lorentz–Debye shape, and we argue in the following that our finding is generic for molecular fluids. Upon decreasing frequency, the onset of friction is followed by liquid-specific behaviour over several decades in time until the hydrodynamic value \( \zeta_0 \) is established: in water, our results for the friction \( \zeta(\omega) \) exhibit a local maximum at \( \omega/2\pi \approx 5 \text{ THz} \), followed by a slow increase towards the limiting value \( \zeta_0 \), which is reached near frequencies of 0.1 THz. For the LJ fluid, \( \zeta(\omega) \) varies more smoothly with a global maximum at an intermediate frequency, and \( \zeta_0 \) is approached slowly from above in accord with the hydrodynamic square-root singularity [Eq. (18)], essentially calculated by Stokes already\(^\text{17}\). On theoretical grounds, this feature of \( \zeta(\omega) \) is generic for all liquids, yet it is suppressed in our data for the other two liquids due to a small prefactor. In the supercooled liquid, we observe a scale separation by three dynamic decades of (i) the rapid onset of friction and (ii) the slow emergence of the hydrodynamic limit. The second process is associated with cage relaxation, strongly delayed in the glassy state, which suggests that the driving mechanism behind

Fig. 2 Flow chart of the data analysis. Along the upper route, one starts from the mean-square displacement (MSD) and computes the generalised mobility \( \tilde{J}(\omega) \) by numerical differentiation and a suitable Fourier transform \( \mathcal{F} \) (adapted Filon algorithm, Eq. (22)); the dynamic friction \( \zeta(\omega) \) follows via Eq. (7). A Fourier backtransform then yields the memory function \( \gamma(t) \). The latter can be obtained more directly along the lower route, which is based on the velocity autocorrelation function (VACF) \( Z(t) \) and employs a deconvolution in time domain (Eq. (23)).

Fig. 3 Dynamic friction and generalised mobility of three prototypical liquids. Columns show simulations results for a mono-atomic fluid, liquid water, and a supercooled liquid. The dynamic friction (red) is obtained from the memory kernel \( \tilde{\gamma}(\omega) \) as depicted in Fig. 2, with the mean-square displacement (MSD, not shown) as initial input. a–c The dynamic friction (red) is obtained from the memory kernel \( \tilde{\gamma}(\omega) \) as depicted in Fig. 2, with the mean-square displacement (MSD, not shown) as initial input. a–c The dynamic friction (red) is obtained from the memory kernel \( \tilde{\gamma}(\omega) \) as depicted in Fig. 2, with the mean-square displacement (MSD, not shown) as initial input.
Friction depends on the coupling of fast and slow processes. The obtained data of $\xi(\omega)$ cover the full range of the dynamic response, thereby connecting physics at different scales. Before discussing the remaining panels (d–l) of Fig. 3, we rationalise key features of $\xi(\omega)$ by tracing their origins to the dynamics of the fluid particles at short and long times (going backwards in Fig. 2). The relevant properties are prominently visible in the second derivative of the MSD, the velocity autocorrelation function (VACF), $Z(t) := \overline{\gamma(t)/\gamma(0)}$, after numerical differentiation with respect to the lag time $t$ (Fig. 4a–c). The following should be contrasted to Ornstein’s model for Brownian motion, employing a single exponential decay of velocity correlations, $Z(t) \approx \gamma_0^2 \exp(-\zeta t/m)$, which implies a constant (Markovian) friction, $\xi(\omega) = \zeta_0$; by $\gamma_0$, we denote the thermal velocity, and $m$ is the molecular mass. As a distinct feature of molecular fluids, obeying Newton’s equations, the VACF’s true short-time decay is parabola-shaped, $Z(t \rightarrow 0) \approx m \gamma_0^2 (1 - \omega^2 t^2/2)$, introducing the Einstein frequency $\omega_0$. For dense liquids, the VACF, after a sign change, generally displays a regime of anti-correlations, which reflect the transient caging by neighbouring molecules (Fig. 1c). For water and the supercooled liquid, these anti-correlations relax slowly with an intermediate power-law decay, $Z(t) \sim t^{-5/2}$ (insets of Fig. 4b, c); such a decay was observed earlier in supercooled liquids and it is a well-established long-time tail in colloidal suspensions and for diffusion in an arrested, disordered environment.

The famous long-time tail encoding hydrodynamic memory, $Z(t \rightarrow \infty) \sim t^{-3/2}$, is clearly developed in our data for the LJ fluid after another sign change (inset of Fig. 4a), and in this situation, Stokes’s hydrodynamics describes the slow motion of single molecules (Fig. 3a). For the other two liquids studied, the tail is not visible in our data due to a small prefactor, which following mode-coupling arguments decreases as either viscosity or diffusivity increases.

The dynamic friction is closely linked to the complex-valued, generalised mobility $\gamma(\omega)$ via $\xi(\omega) = \text{Re}[\gamma(\omega)^{-1}]$. This mobility encodes the response to a small, oscillatory force and is accessible in, e.g., scattering experiments. Here, we computed $\gamma(\omega)$ from the VACF upon employing a fluctuation–dissipation relation (see “Methods” and Fig. 3d–l). Our data reveal a generic, rapid decrease of the dissipative part, $\gamma'(\omega) := \text{Re} \gamma(\omega)$, upon increasing frequency towards the microscopic regime, $\omega \gg \omega_c$; concomitantly, the elastic response, $\gamma''(\omega) := \text{Im} \gamma(\omega)$, has a resonance near $\omega_c$ due to vibrational motion of molecules in their cages. In the low-frequency limit, the reciprocal of the macroscopic friction is recovered, $\gamma'(\omega \rightarrow 0) = 1/\zeta_0$. In the examples studied, both regimes are separated by at least two decades in time, which show material-specific features: the mobility of water molecules is 2.5-fold enhanced over its macroscopic value near $\omega/2\pi \approx 1.3$ THz; similarly, a factor of 30 is observed for the supercooled liquid. At variance, the hydrodynamic long-time tail, as for the LJ liquid, demands $\gamma'(\omega \rightarrow 0)$ to be approached from below. The interplay of slow and fast processes enters the response $\gamma(\omega)$, and thus the dynamic friction $\xi(\omega)$, at all frequencies, which is borne out by the Kramers–Kronig relations. In particular, non-analytic behaviour of $\gamma''(\omega)$ as $\omega \rightarrow 0$ influences the detailed onset of friction at large frequencies.

**Fig. 4 Velocity autocorrelators and corresponding memory functions for the three investigated liquids.** Columns show results for a mono-atomic fluid, liquid water, and a supercooled liquid. a–c simulation results for the velocity autocorrelation function (VACF, brown symbols) display a parabolic decrease at short times (grey lines) and power-law decays at long times (insets, negative values are dotted). The VACF is obtained from the second derivative of the mean-square displacement with respect to lag time. d–f The memory function $\gamma(t)$ encodes the autocorrelation of Brownian forces on the molecules (Eq. (2)). For each liquid, $\gamma(t)$ was computed from a cosine transform of $\xi(\omega)$ [blue lines, Eq. (9)] with input data from Fig. 3a–c and is compared to the deconvolution results in time domain (orange lines, Eq. (23)). The data follow the predicted short-time decay Eq. (16) (grey lines) and exhibit power-law decays consistent with Eq. (19) (insets), preceded by an ultra-slow decay in case of the supercooled liquid (f).

The origin of friction is non-local in time. The rapid decrease of $\gamma''(\omega)$ is mathematically justified from the short-time properties of the VACF. Physical molecular trajectories, being solutions to Newton’s equations, are smooth and yield a smooth function $Z(t)$;...
in particular, all derivatives \( Z^{(n)}(t) \) exist at \( t = 0 \) and are finite. Thus, invoking exact sum rules [Eq. (10)], all moments of the spectrum \( \tilde{\gamma}(\omega) \) are finite, which requires an exponentially fast decay as \( \omega \to \infty \). (This is a special case of a more general characterisation of exponentially decaying probability measures.)

Combining with the large-\( \omega \) asymptote of the imaginary part, \( \tilde{\gamma}''(\omega) \approx 1/\omega_0^2 \) and \( \gamma''(\omega) \approx \gamma''(\omega)/[\gamma''(\omega)^2 + \gamma''''(\omega)^2] \) proves that \( \gamma(\omega) \approx \omega_0^2 \gamma''(\omega) \) as \( \omega \to \infty \) and thus an exponentially fast suppression of the friction.

We stress further that such behaviour is not contained in representations of \( \gamma(\omega) \) as a truncated continued fraction.

It is tempting to use a systematic short-time expansion of \( Z(t) \) to predict the large-frequency behaviour of the friction. However, \( Z(t) \) being an even function due to time-reversal symmetry in equilibrium renders the large-\( \omega \) asymptotes zero, \( \gamma''(\omega) \equiv 0 \) and thus \( \gamma(\omega) \equiv 0 \), even if the complete Taylor series of \( Z(t) \) in \( t = 0 \) was known (see “Methods”). Note that \( \gamma''(\omega) \) and the elastic counterpart of \( \gamma(\omega) \) are well captured by such an expansion (Fig. 3d–f). This observation underlines that, on all scales, friction emerges as a phenomenon that is non-local in time, i.e., it cannot be anticipated from the local behaviour of the molecular trajectories.

Our numerical and theoretical findings are supported by an analytically solvable example. The choice \( Z(t) = \nu_0^2 [1 + (t/\tau)^2]^{-1} \) combines the smoothness and time-reversal symmetry of molecular autocorrelation functions with a long-time tail. It yields an exponential decay of the mobility, \( \gamma''(\omega) = (\pi \tau/2m) e^{-\omega^2} \) (dissipative part), and hence a rapid suppression of friction, \( \gamma(\omega \to \infty) \sim \omega^2 e^{-\omega^2} \), as demanded above (see “Methods” and Fig. 5).

Irreversible momentum transfer drives the onset of friction. A pressing question is about the physical mechanism that generates the onset of friction. Motivated by our results for the supercooled liquid (Fig. 3c), we performed a control simulation for the L-J fluid with the structural relaxation switched off by pinning all particles but one. The rattling motion in such a frozen-in cage (Fig. 2) experiences a dynamic friction that closely resembles our generic findings for \( \gamma(\omega) \) at high frequencies, \( \omega \gtrsim \omega_c \) (Fig. 6). Upon decreasing frequency from \( \omega_c \) to zero, the two dynamics deviate strongly as is most evident in the elastic response: whereas \( \text{Im} \gamma(\omega) \) decreases for the unconstrained fluid and exhibits a zero crossing enforced by hydrodynamics [Eq. (17) and Fig. 3a], it remains positive for the pinned case and grows as \( \text{Im} \gamma(\omega \to 0) \sim 1/\omega \), reminiscent of what one obtains for an Ornstein–Uhlenbeck (OU) particle in a harmonic trap. For even smaller frequencies, \( \omega \lesssim \tau_\eta^{-1} \), the dissipation diverges too, approximately as \( \omega(\omega \to 0) \sim \omega^{1/2} \), which we attribute to the irregular shape of the confining cages; for the OU model with harmonic confinement, \( \gamma(\omega) \approx \text{const} \). At high frequencies, however, the confinement is not relevant, and we conclude that it is the fast, yet irreversible momentum transfer to neighbouring molecules that drives the onset of friction. This is corroborated by the observation that instantaneous momentum exchange implies a non-zero limit, \( \gamma(\omega \to \infty) > 0 \), as in the case of hard spheres.

The fact that dissipation is linked to trajectories for which the time-reversed path is extremely improbable leads us to speculate that the onset frequency \( \omega_c \) is intimately related to the largest Lyapunov exponent \( \lambda_{\text{max}} \) of the fluid, which is close to, but different from the Einstein frequency \( \omega_0 \) (Posch & Hoover).
Discussion

Based on theoretical arguments and corroborated by simulation data that cover up to three orders in magnitude and 4 decades in frequency, we have shown that the friction $\zeta(\omega)$ in molecular liquids emerges rapidly at a large, liquid-specific frequency $\omega_c$ from the time-reversible motion of the atoms. This onset of friction is driven by the irreversible momentum transfer to neighbouring molecules, but also influenced by the slowest processes at hydrodynamic scales. The exponentially fast decay of dissipation spectra such as $\zeta(\omega)$ is easily shadowed by approximations, and as a modelling constraint it is under-investigated in the existing microscopic theories of liquids. The observation that the high-frequency behaviour of $\zeta(\omega)$ is reproduced by the motion of a single particle in an immobile cage refines the question on the quantitative link between friction and microscopic chaos. Concretely: whether and how does the frequency dependence of transport coefficients relate to the Lyapunov spectrum of the liquid?\textsuperscript{23,24}

Going beyond the dynamics of single molecules and their friction, the relation to the visco-elastic properties of complex fluids is of ongoing interest for the physics of polymers, living cells, and the glass transition. The potentially tight coupling between single-particle and collective responses was phrased as an ad hoc extension of Stokes’s friction law to the frequency domain, $\zeta(\omega) = 6\eta \Re [\eta(\omega)]$, referred to as generalised Stokes–Einstein relation (GSER), which has found wide applications in the context of micro rheology experiments.\textsuperscript{18–21} It links the dynamic friction $\zeta(\omega)$ of a probe particle to the macroscopic shear modulus $G(\omega) = -i\omega\eta(\omega)$, a complex-valued function encoding the stress response of the macroscopic fluid sample to a small, oscillatory shear strain. The generalised viscosity $\eta(\omega)$ tends to the hydrodynamic shear viscosity $\eta_0$ as $\omega \to 0$, with $\Re \eta(\omega)$ representing the spectrum of shear stress fluctuations (up to a constant factor) by a fluctuation–dissipation relation. Thus, if the GSER holds the single-particle memory $\gamma(t)$ is proportional to the autocorrelator of shear stresses, which means that the Brownian force on the particle and the fluctuation of the shear stress are statistically equivalent variables.

A critical assessment of the validity of the GSER is permitted by comparing our data for $\zeta(\omega)$ to results for $\eta(\omega)$, calculated within the same simulations (see Fig. 7 and “Methods”). Generically, the dissipative part, $\Re [\eta(\omega)]$, decays exponentially fast as $\omega \to \infty$, which is required by analogous arguments as given for $\zeta(\omega)$ and $\gamma(t)$. For high frequencies, only the imaginary part...
survives to its slow decay, \( \hat{\eta}(\omega) \approx G_{\infty}/(-i\omega) \), inducing a non-zero and real-valued modulus, \( G_{\omega} \gg \omega \), \( G_{\infty} \gg 0 \). Therefore, our data clearly demonstrate that, indeed, liquids respond to high-frequency shear like a non-dissipative, elastic solid as put forward by the classical work of Frenkel. However, the attempt to predict the elastic modulus \( G_{\infty} \) from the vibrational motion of molecules in their cages, by virtue of the GSER, would considerably overestimate the modulus by factors of \( \approx 2 \) for the three liquids studied (Fig. 7d–f). In passing, we note that Maxwell’s model for viscoelasticity predicts \( \hat{\eta}(\omega) \approx G_{\infty}/(1 - i\omega\tau) \) with some relaxation time \( \tau \), breaks down at high frequencies as it implies a slowly decaying real part, \( \Re\hat{\eta}(\omega \to \infty) \sim \omega^{-2} \), in sharp contrast to exact sum rules and to the exponentially fast decay for molecular liquids. Therefore, treatments of sound-like, elastic waves on the footing of this and similar models appear incomplete.

The passage from the elastic to the viscous limit occurs upon decreasing frequency, leading in case of the LJ fluid to a monotonic increase of \( \Re\hat{\eta}(\omega) \), which, empirically, follows a compressed exponential over almost the full frequency domain (Fig. 7a). In particular, \( \hat{\eta}(\omega) \approx \eta_0 \) is constant for \( \omega \approx 2\tau_\text{c}^{-1} \), which defines the hydrodynamic regime. For these frequencies, the single-molecule response is very well described by Stokes’s dynamic friction [Eq. (18)], making the GSER violation apparent for Newtonian fluids, for which \( \hat{\eta}(\omega) = \eta_0 \). It is evidenced further by the dissimilarity of the elastic parts, \( \Im\hat{\eta}(\omega) \) and \( \Im\hat{\eta}(\omega) \).

For water, the viscosity and friction spectra share similar features and coincide fairly well (Fig. 7b), including the elastic parts. Thus, the GSER serves as a reasonable qualitative description, in particular for frequencies below \( \approx 2 \) THz, i.e., slower than the vibrations of the first hydration shell. In supercooled liquids, the Stokes–Einstein relation for molecules (i.e., the GSER for \( \omega \to 0 \)) holds in the presence of a huge variation of the viscosity. In particular, the ratio \( \omega_0/\eta_0 \) is observed to be constant over a wide temperature range—indeed in agreement with the mode-coupling theory of the idealised glass transition. At very low temperatures, however, marked deviations from the Stokes–Einstein relation (mostly studied for \( \omega \to 0 \)) have received considerable attention as they signify the opening of additional relaxation channels not included in the standard theory. For the moderately supercooled liquid studied here exemplarily, both viscous and elastic responses satisfy the GSER over a wide frequency window (Fig. 7c). Notably, the elastic components collapse almost perfectly in this case, \( \Im\hat{\eta}(\omega) \sim \Im\hat{\eta}(\omega) \), which we attribute to the same (apparent) power-law scaling, \( \omega \approx \omega_0^{0.75} \), at intermediate frequencies. Yet, the collective response lacks the elastic peak of \( \Im\hat{\eta}(\omega) \) at \( \omega_0 \), causing the breakdown of the GSER at large frequencies. This suggests that a future frequency-resolved study of systematic deviations from the GSER upon further supercooling can clarify the separate contributions of fast and slow processes to the decoupling of diffusion and viscosity (“Stokes–Einstein violation”) close to the glass transition temperature.

We conclude that molecular friction in liquids arises from a complex interplay of processes on very disparate time scales. The large variability of \( \langle \omega \rangle \) observed over orders of magnitude reveals the strongly non-Markovian nature of Brownian motion in any liquid environment, with far-reaching implications for nanoscale processes. Examples are as diverse as reaction rates and barrier crossings in macromolecular dynamics and flows near liquid–solid interfaces; the ability to quantify the corresponding memory is vital for their realistic descriptions. From a numerical point of view, our ansatz-free approach has immediate applications to and extends current methods for the analysis of high-resolution microelectrode data, which involves deducing frequency-dependent moduli from the displacement statistics along the same lines as done here for the dynamic friction. Relying merely on the existence of a steady state [Eq. (12)], the developed methodology is not limited to friction, but can be transferred to the analysis of non-Markovian time series from simulation and experiment. It finds novel uses in, e.g., the anomalous diffusion within living cells and the kinetics of chemical reactions. It opens a promising avenue for research on the migration of malignant cells in tissue and on predictive stochastic models of financial market and geographic data.

**Methods**

**Generalised Langevin equation.** A labelled fluid particle of mass \( m \), position \( \mathbf{r}(t) \), and momentum \( \mathbf{p}(t) = m\dot{\mathbf{r}}(t) \) obeys the generalised Langevin equation (GLE) [8]:

\[
\dot{\mathbf{r}}(t) = -\int_0^t ds \, (\mathbf{r}(t - s) - \mathbf{r}(t)) + \xi(t),
\]

where the Brownian force \( \xi(t) \) is a stochastic process with zero mean and covariance

\[
\langle \xi(t) \xi(t') \rangle = mk_B T \langle |t - t'| \rangle,
\]

satisfying the fluctuation–dissipation theorem. Rewriting Eq. (1) for the velocity autocorrelation function (VACF), \( \xi(t) = (\mathbf{p}(t) - \mathbf{p}(0))/\langle \mathbf{p}(t) \rangle \), describing momentum relaxation, yields

\[
\dot{V}(t) = -\int_0^t ds \, y(t - s) Z(s), \quad Z(0) = k_B T/m.
\]

Its Fourier–Laplace transform [Eq. (8)] provides the link to and the definition of the (complex-valued) memory kernel \( \hat{\mathcal{Y}}(\omega) \),

\[
\hat{Z}(\omega) = \frac{k_B T/m}{\omega - \hat{\mathcal{Y}}(\omega)}.
\]

**Linear response.** For a mass \( m \) driven by a periodic force \( F(t) = F_0 \cos(\omega t) \) with frequency \( \omega \) and amplitude \( F_0 \), the stationary response \( \dot{\mathbf{r}}(t) \), averaged over many realisations of the experiment, is given by

\[
\frac{d}{dt} \mathcal{V}(t) = F(t) - \int_{-\infty}^{t} m y(t - s) \dot{\mathbf{r}}(s) ds,
\]

corresponding to Eq. (1) after shifting the lower integral boundary to \(-\infty\) to ensure relaxation of transients. The upper boundary can be shifted to \(+\infty\) with the convention that the response function \( \mathcal{Y}(t < 0) = 0 \). By linearity of the equation, the solution is of the form \( \mathcal{V}(t) = \Re[e^{i\omega t}\mathcal{Y}(\omega)] \) with complex amplitude \( \mathcal{Y}_\omega \) and inserting into Eq. (5) yields \( \dot{\mathcal{Y}}(\omega) = \mathcal{Y}(\omega) F_0 \) in terms of the generalised mobility,

\[
\dot{\mathcal{Y}}(\omega) = \left[-i\omega m + \mathcal{Y}(\omega)\right]^{-1},
\]

also referred to as complex-valued admittance. Its central ingredient is the one-sided Fourier transform of the response function, \( \mathcal{Y}(\omega) = \int_{0}^{\infty} e^{-i\omega t} \dot{\mathcal{Y}}(t) dt \). Comparing to Eq. (4), which describes equilibrium correlations, yields the fluctuation–dissipation relation:

\[
\dot{\mathcal{Y}}(\omega) = \frac{k_B T}{\pi m} \mathcal{Y}(\omega),
\]

Friction describes the resistance to a prescribed velocity, as in Stokes’s pendulum experiments. Thus, inverting the above argument, the force response to an oscillatory velocity \( \mathbf{v}(t) = v_x \cos(\omega t) \) with complex amplitude \( \mathcal{Y}_\omega \) and we identify \( \dot{\mathcal{Y}}(\omega)^{-1} \) as a generalised friction. However, merely the real part describes dissipation and deserves to be called a friction, which is seen from the mean dissipated power:

\[
T_0 \frac{1}{2} \int_{0}^{\infty} \dot{\mathcal{Y}}(\omega) F(\omega) \mathcal{V}(\omega)^2 \sin^2(\omega t) dt = \frac{1}{2} Re \{\mathcal{Y}(\omega)^{-1}\} \mathcal{Y}(\omega)^2/2, \text{ averaged over a full cycle of length } T_0 = 2\pi/\omega.
\]

We set the dynamic friction as

\[
\xi(\omega) = \Re \{\mathcal{Y}(\omega)^{-1}\} = m Re \{\hat{\mathcal{Y}}(\omega)\},
\]

in particular, \( \xi(\omega) \approx 0 \). This is in line with the conventional (Markovian) Langevin equation, \( \mathcal{Y}(\omega) = -(\xi_0/m) \mathcal{Y}(\omega) + \xi(\omega) \). There, the response is governed by

\[
\dot{\mathcal{Y}}(\omega) = \left[-i\omega m + \xi_0 + \xi_0 \right]^{-1}, \text{ implying a static friction, } \xi(\omega) = \xi_0.
\]

Equations (6) and (7) and (and variants thereof) are the basis of (passive) microelectrode experiments, which use observations of Brownian motion to infer the friction \( \xi(\omega) \) and \( \Im\hat{\mathcal{Y}}(\omega) \) of a probe particle in a complex medium and relate it via the GSER to the local visco-elastic properties. The macroscopic shear viscosity, \( \eta_0 = (k_B T)^2 \int_0^\infty \mathcal{C}_0(t) dt \), is the Green–Kubo integral of the autocorrelation, \( \mathcal{C}_0(t) = (\mathcal{Y}(\omega) + \mathcal{Y}(\omega)^{-1})/V \), of shear stress fluctuations \( \mathcal{Y}(\omega) \), given as an off-diagonal element of the stress tensor; \( \mathcal{V} \) denotes the sample volume. Similarly, via a fluctuation–dissipation relation, the frequency-dependent response coefficient \( \hat{\mathcal{Y}}(\omega) \) to oscillatory shear is the Fourier–Laplace transform [Eq. (8)] of \( \mathcal{C}_0(t)/k_B T \), and thus \( \mathcal{Y}(\omega) = \Re \{\hat{\mathcal{Y}}(\omega)\} \).
Mathematical framework. For the harmonic analysis of the autocorrelation function \( C(t) \) of a stationary time series, we use the Fourier–Laplace transform
\[
\hat{C}(z) = \int_0^\infty e^{zt} C(t) \, dt,
\]
which is well-defined for all frequencies \( z \) in the upper complex plane, \( \Re{z} > 0 \). Along the imaginary axis, \( z = iy \), it recovers the conventional Laplace transform. For real frequencies \( \omega \), the real and imaginary parts of \( \hat{C}(\omega) \) describe physically accessible spectra, which are related to each other by Kramers–Kronig integrals.\(^{53,57} \) For example, \( \Re{C}(\omega) \) for fixed \( \omega \) is determined by the full function \( \Im{C}(\omega) \). The real part is positive, \( \Re{C}(\omega) \geq 0 \), and most importantly, we have the unique Fourier backtransform:
\[
C(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \Re{\hat{C}(\omega)} \, d\omega.
\]
If \( C(t) \) is \( n \)-times continuously differentiable at \( t=0 \), this implies sum rules for the spectrum (\( k=0,1,\ldots,n \)):
\[
\frac{1}{\pi} \int_{-\infty}^{\infty} (-i\omega)^k \Re{\hat{C}(\omega)} \, d\omega = C^{(k)}(0) < \infty.
\]
In equilibrium, only positive frequencies are needed as \( \Re{\hat{C}(\omega)} = \Re{\hat{C}(\omega^*)} \) and the integrals are real-valued.

Next, we introduce a memory function \( C(t) \) solely by invoking results from complex analysis\(^{66} \). \( \hat{C}(z) \) as above is a holomorphic function with \( \Re{C}(\omega) \geq 0 \), i.e., \( \hat{C}(z) \) is of Herglotz–Nevanlinna type, and \( \Im{C}(\omega) \hat{C}(z) \) is bounded in \( \Im{z} \). Suppose that \( C(t) \) has a regular short-time expansion, \( C(t \to 0) = C_0^\prime [+v t - \frac{1}{2} m^2 t^2] \), which implies
\[
\hat{C}(z) \approx C_0 - i\omega C_0^\prime - i\omega^2 C_0^\prime + \cdots.
\]

Suppose \( C(t) \) has a regular short-time expansion, \( C(t \to 0) = C_0^\prime [+v t - \frac{1}{2} m^2 t^2] \), which implies
\[
\hat{C}(z) \approx C_0 - i\omega C_0^\prime - i\omega^2 C_0^\prime + \cdots.
\]

In the context of the VACE, one puts \( C_0 = \int_D \omega^2 = \lambda = \omega \), and \( v = \omega \) and \( m = \omega \) and \( \omega \) infers for the memory kernel \( M(z) = C(z) - i\omega + M(z) \)
\[
M(z) \approx \int_{\Im{z}(t)} \gamma(t) \, dt.
\]

Short-time expansion. The smoothness of physical molecular trajectories, being solutions to Newton’s equations, allows for a short-time expansion of the VACE. Combining with the time-reversal symmetry in equilibrium, \( Z(t) = Z(-t) \), only even powers in \( t \) contribute and one obtains \( Z(t) \approx k_0 T \sum_{\omega} C^2(\omega)/(2\pi) \)
\[
\text{with Taylor coefficients } C_0\text{ given from equilibrium matrix elements of powers of the underlying Liouville operator.}\(^{28} \) To connect with the notion of the memory kernel \( C_0^\prime (\omega) \), \( \omega \) and \( \omega \), \( \omega \), and \( \omega \) of Fourier–Laplace transforming term by term yields the high-frequency expansion of \( \hat{Z}(\omega) \) and thus of \( \hat{Z}(\omega) = (k_0 T)^{-1} \hat{Z}(\omega) \), which is purely imaginary: \( \hat{Z}(\omega \to \infty) \approx \sum_{\omega} C_0 (\omega) [1 + \cdots] \approx \hat{C}(\omega) \). Using Eq. (7), we have
\[
\hat{C}(z) \approx \frac{1}{\pi} \int_{-\infty}^{\infty} e^{-izt} \Re{C(t)} \, dt.
\]

Suppose \( C(t) \) is \( n \)-times continuously differentiable at \( t=0 \), this implies sum rules for the spectrum (\( k=0,1,\ldots,n \))
\[
\frac{1}{\pi} \int_{-\infty}^{\infty} (-i\omega)^k \Re{\hat{C}(\omega)} \, d\omega = C^{(k)}(0) < \infty.
\]

Using Eq. (6), implying for the memory function in time domain:
\[
\gamma(t \to 0) = \omega_0^2 (1 - \omega_0^2 t^2/2) + O(t^4).
\]

Long-time tails. In an unbounded fluid, momentum conservation leads to persistent velocity correlations, \( Z(t \to \infty) \approx v_0^2 (t / \tau_0)^{-1/2} \), which was explained in terms of hydrodynamic backflow and diffusion of a momentum vortex\(^{65,66} \). The tail induces a small-\( \omega \)-singularity in the frequency domain\(^{67} \), which reads for the memory kernel: \( m(t \to \omega) = \omega_0^2 [1 + \cdots] \), see Eq. (4) and the hydrodynamic friction \( \zeta_0 := m(\omega) = k_B T / \int_0^\infty Z(z) \, dz \).

In the framework of the creeping flow equations, Stokes found\(^{47} \)
\[
\zeta(\omega \to 0) \approx \omega_0^2 (1 + \cdots)
\]

\[
\gamma(t \to 0) = \omega_0^2 (1 - \omega_0^2 t^2/2) + O(t^4).
\]

Analytically solvable example. Consider the following analytically tractable model for the VACE:
\[
Z(t) = \frac{v_0^2}{1 + (t/t_f)^2}, \quad v_0^2 = k_B T/m,
\]

\[
\gamma(t \to 0) = \omega_0^2 (1 - \omega_0^2 t^2/2) + O(t^4).
\]

\[
\zeta(\omega \to 0) \approx \omega_0^2 (1 + \cdots)
\]

\[
\gamma(t \to 0) = \omega_0^2 (1 - \omega_0^2 t^2/2) + O(t^4).
\]

In application of theorem 1.2 by Mimica,\(^{44} \) we confirm that
\[
\text{lim}_{\omega \to 0} (\omega^2 - \log(\gamma(Z(\omega))))^+ = \tau_c
\]

\[
\gamma(t \to 0) = \omega_0^2 (1 - \omega_0^2 t^2/2) + O(t^4).
\]

Adapted Filon algorithm. The computation of the frequency-dependent friction requires a robust numerical Fourier transform, for which we developed a physics-enriched version of Filon’s quadrature formula. The goal is to evaluate \( f(\omega) = \int_0^\infty e^{i\omega t} f(t) \, dt \) for a function \( f(t) \) sparsely sampled on an irregular grid \( t_0, t_1, \ldots, t_n \) for an arbitrary set of frequencies \( \omega \). The idea of Filon’s algorithm is to interpolate \( f(t) \) by elementary functions between the grid points (usually parabolas), thereby reducing the Fourier integral to a finite sum of integrals, for which analytic expressions exist. Anticipating that the normal physical decay of correlation functions is exponential, we approximate \( f(t) \approx a e^{-\gamma t} \) in the interval.
with $a_i$ and $y_i$ fixed by $f(x_i)$ and $f(x_{i+1})$. Then,
\[
\int_{t_i}^{t_{i+1}} f(t) \, dt \approx \frac{1}{\Delta t} \left[ e^{-\gamma t_i} + \sum_{k=1}^{\infty} \frac{\gamma^k}{k!} t_i^k \right] 
\]
(22)

Spurious low-frequency oscillations of the transform are removed by smoothly truncating the integral at $t_i$ here by assuming a terminal exponential decay of $f(t)$, which leads to the last term on the r.h.s. of Eq. (22). In order to preserve the short-time properties of $f(t)$ we fit a polynomial in $t^2$ to the first few data points and solve the integral analytically; this improves the high-frequency behaviour of $f(t)$.

The dynamic friction $\zeta(t)$ and the memory function $y(t)$ are obtained from MSD data as follows (Fig. 2): The timescale-dependent diffusion coefficient, $D(t)$, is obtained from numerical differentiation. In all cases studied, it grows out from zero, has a maximum, and converges slowly towards the long-time diffusion constant $D_\infty = D(t \to \infty)$, see Supplementary Fig. 1. Using the above algorithm, we compute $\hat{Z}(t) = D_{\infty} - \int_0^t d\tau \, \hat{y}(\tau)$. Discretising on a uniform time grid, $t_n = \Delta t (n = 0, 1, \ldots)$, and employing the trapezoidal rule for the integral, a recursion relation for $G_\gamma := G(t)$ with the initial value $G_0 = 0$ follows:
\[
G_\gamma = 1 - \frac{\gamma}{D} \sum_{n=1}^{\infty} G_{\gamma-n}, \quad \gamma > 0.
\]
(23)

Going beyond Kowalki et al.36, we introduce a predictor–corrector scheme to stabilise the numerical solutions: In the predictor step, one evaluates $G_n^\gamma$ and $G_{n+1}^\gamma$ from Eq. (23). Afterwards, the weighted average $G_n := (G_n + 3G_n^\gamma + 3G_{n+1}^\gamma)/5$ manifests itself as the corrector step. Results for $G(t)$ can be found in the Supplementary Fig. 2. Finally, the memory function $y(t) := \mathcal{G}(t)$ is obtained by central differences. If one starts from MSD data on a sparse (e.g., geometrically spaced) time grid, a cubic spline interpolation of the MSD in the variable $\xi$ is suitable to sample $Z(t)$ on a uniform grid of up to $10^5$ points.

**Molecular dynamics simulations.** Simulations of liquid water were performed with the GROMACS 5.1 package37 using the SPC/E water model, which was shown to accurately reproduce the linear absorption spectra of water from experiments and ab-initio MD simulations up to frequencies of about 30 THz24. The system of 3007 molecules in a cubic box of linear size 4.49 nm was equilibrated at 300 K and 1 bar following standard procedures38. Correlation functions were obtained from a constant-particle-number, constant-volume, constant-energy (NVE) simulation over 275 ps with the velocity-Verlet integrator and a time step of 1 fs, using double floating-point precision to achieve good energy conservation. The frequency-dependent viscosity was computed from additional NVE runs, totalling to 49 ns.

For the other two liquids, we used the massively parallel software HAL’s MD package39 (version 1.0.6b), permitting the sampling of dynamic correlations on a sparse time grid and featuring smoothly truncated potentials to virtually eliminate any energy drift. The mono-atomic fluid consists of $10^5$ particles interacting pairwise via the LJ potential, $U(r) = 4\varepsilon [ (\sigma/r)^{12} - (\sigma/r)^6 ]$, with $\varepsilon = 520$; a unit of time is defined by $\tau_{LJ} := \sqrt{\sigma^2/\varepsilon}$. Equilibration in the NVE ensemble at number density $n = 0.8$ and thermal energy $k_B T = 1.3$ followed the protocol by Roy et al.34. The supercooled liquid was realised by a Kub-Anderson 80:20 binary mixture32 of 64,000 LJ beads at $q = 1.26$ and $T_n = 2.6$, equilibrated over a time span of 9,000 $\tau_{LJ}$, and we traced the trajectories of the larger particles. The chosen temperature is well below the melting point78, and ab-initio MD simulations up to frequencies of about 30 THz74. The system of 85,079 water molecules was generated with open source software as indicated in the “Methods” section. The source code used to analyse the data for the current study is available from the corresponding author upon reasonable request.

### Data availability

The data sets generated and analysed during the current study are available from the corresponding author upon reasonable request.

### Code availability

Primary data were generated with open source software as indicated in the “Methods” section. The source code used to analyse the data for the current study is available from the corresponding author upon reasonable request.

Received: 25 November 2019; Accepted: 25 May 2020; Published online: 10 July 2020

### References

1. Franosch, T. et al. Resonances arising from hydrodynamic memory in Brownian motion. *Nature* **478**, 8–11 (2011).
2. Kheirotf, S., Simha, A., Melin, K., Li, T. & Raizen, M. G. Observation of Brownian motion in liquids at short times: instantaneous velocity and angular loss. *Science* **333**, 1493–1496 (2014).
3. Berner, J., Müller, B., Gomez-Solano, J. R., Krüger, M. & Béchinger, C. Oscillating modes of driven colloids in overdamped systems. *Nat. Commun.* **9**, 999 (2018).
4. Linder, L., Nöhr, C. & Bäumer, F. The dielectric properties of the liquid at very low frequencies. *Phys. Chem. Chem. Phys.* **17**, 375–377 (2015).
5. de Sancho, D., Sirur, A. & Best, R. B. Molecular origins of internal friction effects on protein-folding rates. *Nat. Commun.* **5**, 4307 (2014).
6. Daldrop, J. O., Kappler, J., Brüning, F. N. & Netz, R. R. Butane dihedral angle dynamics in water is dominated by internal friction. *Proc. Natl Acad. Sci. USA* **115**, 5169–5174 (2018).
7. Sollich, P., Lequeux, F., Hébraud, P. & Cates, M. E. Rheology of soft glassy materials. *Phys. Rev. Lett.* **108**, 205701 (2012).
8. Winter, D., Horbach, J., Virnau, P. & Binder, K. Dynamic arrest in multicomponent glass-forming alloys. *Phys. Rev. Lett.* **104**, 195701 (2010).
9. Winter, D., Horbach, J., Virnau, P. & Binder, K. Active nonlinear microphysics in a glass-forming Yukawa fluid. *Phys. Rev. Lett.* **108**, 028303 (2012).
10. Höfling, F. & Franosch, T. Anomalous transport in the crowded world of biological cells. *Rep. Prog. Phys.* **76**, 046602 (2013).
11. Becchi, E. et al. Massively parallel, fully adaptive flow slippage in carbon nanotubes. *Nature* **537**, 210–213 (2016).
12. Perakis, F. et al. Coherent X-rays reveal the influence of cage effects on ultrafast water dynamics. *Nat. Commun.* **9**, 1917 (2018).
13. Gaspard, P. et al. Experimental evidence for microscopic chaos. *Nature* **394**, 685–688 (1998).
14. Bartis, A., Rätzke, K., Meyer, A. & Faupel, F. Dynamic arrest in multicomponent glass-forming alloys. *Phys. Rev. Lett.* **104**, 195701 (2010).
15. Hansen, J.-P. & McDonald, I. *Theory of Simple Liquids* (Academic Press, Amsterdam, 2006).
16. Stokes, G. O. On the effect of the internal friction of fluids on the motion of a pendulum. *Trans. Camb. Philos. Soc.* **9**, 8 (1851).
17. Mason, T. G. & Netz, R. R. Optical measurements of frequency-dependent linear viscoelastic moduli of complex fluids. *Phys. Rev. Lett.* **74**, 1250–1253 (1995).
18. Gittes, F., Schnurr, B., Olimsted, P. D., MacKintosh, F. C. & Schmidt, C. F. Microscopic viscoelasticity: shear moduli of soft materials determined from thermal fluctuations. *Phys. Rev. Lett.* **79**, 3286–3289 (1997).
19. Squires, T. M. & Mason, T. G. Fluid mechanics of active cytoskeletal networks. *Science* **315**, 370–373 (2007).
20. Dorfman, R. An Introduction to Chaos in Nonequilibrium Statistical Mechanics (Cambridge University Press, 2003).
21. Höfling, F. & Franosch, T. Anomalous transport in the crowded world of biological cells. *Rep. Prog. Phys.* **76**, 046602 (2013).
22. Mason, T. G. & Netz, R. R. Optical measurements of frequency-dependent linear viscoelastic moduli of complex fluids. *Phys. Rev. Lett.* **74**, 1250–1253 (1995).
23. Dorfman, R. An Introduction to Chaos in Nonequilibrium Statistical Mechanics (Cambridge University Press, 2003).
24. Cohen, E. D. G. Transport coefficients and Lyapunov exponents. *Phys. A* **213**, 293–314 (1994).
25. Posch, H. A. & Hoover, W. G. Lyapunov instability of dense Lennard-Jones fluids. *Phys. Rev. A* **38**, 473–482 (1988).
26. Zwanzig, R. Time-correlation functions and transport coefficients in statistical mechanics. *Annu. Rev. Phys. Chem.* **16**, 67–102 (1965).
27. Mori, H. Transport, collective motion, and Brownian motion. *Prog. Theor. Phys.* **33**, 423–455 (1965).
28. Ailawadi, N. K., Rahman, A. & Zwanzig, R. Generalized hydrodynamics and analysis of current correlation functions. Phys. Rev. A 4, 1616–1625 (1971).
29. Boquet, L., Piascki, J. & Hansen, J.-P. On the Brownian motion of a massive sphere suspended in a hard-sphere fluid. I. Multiple-time-scale analysis and microscopic expression for the friction coefficient. J. Stat. Phys. 76, 505–526 (1994).
30. Shin, H. K., Kim, C., Talkner, P. & Lee, E. K. Brownian motion from molecular dynamics. Chem. Phys. 375, 316 – 326 (2010).
31. Lesnicki, D., Vuilleumier, R., Carof, A. & Rotenberg, B. Molecular hydrodynamics from memory kernels. Phys. Rev. Lett. 116, 148704 (2016).
32. Jung, G., Hanke, M. & Schmidt, F. Iterative reconstruction of memory kernels. J. Chem. Theory Comput. 13, 2481–2488 (2017).
33. Meyer, H., Voigtmann, T. & Schilling, T. On the non-stationary generalized Langevin equation. J. Chem. Phys. 147, 214110 (2017).
34. Kowalik, B. et al. Memory-kernel extraction for different molecular solutes in solvents of varying viscosity in confinement. Phys. Rev. E 100, 012126 (2019).
35. Tassiari, M., Evans, R. M. L., Warren, R. L., Bailey, N. J. & Cooper, J. M. Micro rheology with optical tweezers: data analysis. New J. Phys. 14, 115032 (2012).
36. Nishi, K., Kilfoil, M. L., Schmidt, C. F. & MacKintosh, F. C. A symmetrical method to obtain shear moduli from micro rheology. Soft Matter 14, 3716–3723 (2018).
37. Fuchs, M., Götz, W. & Mayr, M. R. Asymptotic laws for tagged-particle motion in glassy systems. Phys. Rev. E 58, 3384–3399 (1998).
38. Götz, W. Complexes of Glass-Forming Liquids: A Mode-Coupling Theory. International Series of Monographs on Physics (Oxford University Press, Oxford, 2009).
39. Williams, S. R., Bryant, G., Snook, I. K. & van Megen, W. Velocity autocorrelation function in supercooled liquids: Long-time tails and anomalous shear-wave propagation. Phys. Rev. E 94, 060601 (2016).
40. Ackerson, B. J. & Fleishman, L. Correlations for dilute hard core suspensions. J. Chem. Phys. 76, 2675–2679 (1982).
41. Fuchs, M. & Kroy, K. Statistical mechanics derivation of hydrodynamic boundary conditions: the diffusion equation. J. Phys.: Condens. Matter 14, 9223 (2002).
42. Mandal, S., Schrack, L., Löwen, H., Sperl, M. & Franosch, T. Persistent anti-correlations in Brownian dynamics simulations of dense colloidal suspensions revealed by noise suppression. Phys. Rev. Lett. 123, 168001 (2019).
43. van Beijeren, H. Transport properties of stochastic Lorentz models. Rev. Mod. Phys. 54, 195–234 (1982).
44. Hiyong, T. & Franosch, T. Crossover in the slow decay of dynamic correlations in the Lorentz model. Phys. Rev. Lett. 98, 140601 (2007).
45. Alder, B. J. & Wainwright, T. E. Velocity autocorrelations for hard spheres. Phys. Rev. Lett. 18, 988–990 (1967).
46. Ernst, M. H., Hauge, E. H. & van Leeuwen, J. M. J. Asymptotic time behavior of correlation functions. Phys. Rev. Lett. 25, 1254–1256 (1970).
47. Arbe, A., Maldon de Molina, P., Alvarez, F., Frick, B. & Colmenero, J. Dielectric susceptibility of liquid water: microscopic insights from coherent and incoherent neutron scattering. Phys. Rev. Lett. 117, 185501 (2016).
48. Mimica, A. Exponential decay of measures and Tauberian theorems. J. Math. Anal. Appl. 440, 266–285 (2016).
49. Boon, J. P. & Yip, S. Molecular Hydrodynamics. (Dover Publications, Inc., New York, 1991).
50. Frenkel, J. Kinetic Theory of Liquids. (Oxford Univ. Press, London, 1946).
51. Schulz, J. C. F., Schlach, A., Heyden, M., Netz, R. R. & Kappler, J. Molecular interpretation of the non-Newtonian viscoelastic behavior of liquid water at high frequencies. https://arxiv.org/abs/2003.08309 [physics.fl-dyn].
52. Tarjus, G. & Kivelson, D. Breakdown of the Stokes–Einstein relation in supercooled liquids. J. Chem. Phys. 103, 3071–3073 (1995).
53. Kumar, S. K., Szamel, G. & Douglas, J. F. Nature of the breakdown in the Stokes–Einstein relationship in a hard sphere fluid. J. Chem. Phys. 124, 214505 (2006).
54. Gupta, S. et al. Validity of the Stokes–Einstein relation in soft colloids up to the glass transition. Phys. Rev. Lett. 115, 128302 (2015).
55. Dehouai, A., Issenmann, B. & Caupin, F. Viscosity of deeply supercooled water and its coupling to molecular diffusion. Proc. Natl Acad. Sci. U.S.A. 112, 12020–12025 (2015).
56. Parmar, A. D. S., Sengupta, S. & Sastry, S. Length-scale dependence of the Stokes–Einstein and Adam–Gibbs relations in model glass formers. Phys. Rev. Lett. 119, 055501 (2017).
57. Ko, J., Sinha, A. & Raizen, M. G. Brownian motion as a new probe of wettability. J. Chem. Phys. 146, 134707 (2017).
58. Huang, K. & Sriluksana, L. Effect of interfaces on the nearby Brownian motion. Nat. Commun. 6, 8558 (2015).
59. Dessau, L. & Barrat, J. L. Flow boundary conditions from nano- to micro-scales. Soft Matter 3, 685 (2007).
60. Herrera-Delgado, E., Perez-Carrasco, R., Briscoe, J. & Sollich, P. Memory functions reveal structural properties of gene regulatory networks. PLoS Comput. Biol. 14, e1006003 (2018).
61. Karamata, J. Neuer Beweis und Verallgemeinerung der Tauberschen Sätze, welche die Laplace- und Stieltjes-Transformation betreffen. J. Reine Angew. Math. 164, 27–39 (1931).
62. Cornfeld, N. Behavior of autocorrelation functions. Phys. Rev. A 6, 1570–1573 (1972).
63. Roy, S., Dietrich, S. & Höhfeld, F. Space resolved dynamics of a tracer in a disordered solid. J. Non-Cryst. Solids 357, 472–478 (2011).
64. Hess, B., Kutzner, C., Van Der Spoel, D. & Lindahl, E. Gromacs 4: algorithms and architectural developments. J. Chem. Theory Comput. 4, 335–447 (2008).
65. Hess, B., Kutzner, C., Van Der Spoel, D. & Lindahl, E. Gromacs 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation. J. Chem. Theory Comput. 4, 335–447 (2008).
66. Roy, S., Dietrich, S. & Höhfeld, F. Highly accelerated simulations of glassy dynamics using GPUs: caveats on limited floating-point precision. Comput. Phys. Commun. 182, 1120–1129 (2011).
67. Hess, B., Kutzner, C., Van Der Spoel, D. & Lindahl, E. Gromacs 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation. J. Chem. Theory Comput. 4, 335–447 (2008).
68. Roy, S., Dietrich, S. & Höhfeld, F. Structure and dynamics of binary liquid mixtures near their continuous demixing transitions. J. Chem. Phys. 145, 134505 (2016).
69. Roy, S., Dietrich, S. & Höhfeld, F. Structure and dynamics of binary liquid mixtures near their continuous demixing transitions. J. Chem. Phys. 145, 134505 (2016).
70. Pedersen, U. R., Schroder, T. B. & Dyre, J. C. Phase diagram of the supercooled Lennard-Jones mixtures. Phys. Rev. Lett. 120, 165501 (2018).

Acknowledgements
F.H. is indebted to Thomas Franosch for introducing him to the field of complex transport. We benefited from discussions with Lydéric Bocquet, Matthias Fuchs, Julian Kappler, and Klaus Kroy. This research has been funded by Deutsche Forschungs gemeinschaft (DFG, German Research Foundation) through the grant SFB 1114 (project ID: 235221381, subprojects B03 and C01) and under Germany’s Excellence Strategy–MATH+: The Berlin Mathematics Research Centre (EXC-2046/1–project ID: 390685688 [subproject E4–4]). Further funding by the European Research Council (ERC Advanced H 2020 Grant “NoMaMemo”) is gratefully acknowledged. Some of the data were produced with the supercomputer “Lise” (HLRN-IV) of the North-German Supercomputing Alliance.

Author contributions
A.S., R.N., and F.H. conceived the project and wrote the manuscript. B.K. and F.H. analysed the data. A.S. carried out the analytical work. All authors discussed the results and implications and commented on the manuscript at all stages.
Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s42005-020-0389-0.

Correspondence and requests for materials should be addressed to F.H.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.