Splitting of the Universality Class of Anomalous Transport in Crowded Media

Markus Spanner,1 Felix Höfling,2,3 Sebastian C. Kapfer,1 Klaus R. Mecke,1 Gerd E. Schröder-Turk,1 and Thomas Franosch5,6

1Institut für Theoretische Physik, Friedrich-Alexander-Universität Erlangen–Nürnberg, Staudtstraße 7, 91058 Erlangen, Germany
2Fachbereich Mathematik und Informatik, Freie Universität Berlin, Arnimallee 6, 14195 Berlin, Germany
3Max-Planck-Institut für Intelligente Systeme, Heisenbergstraße 3, 70569 Stuttgart, Germany, and IV. Institut für Theoretische Physik, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany
4Murdoch University, School of Engineering and IT, Mathematics and Statistics, Murdoch, Western Australia 6150, Australia
5Institut für Theoretische Physik, Leopold-Franzens-Universität Innsbruck, Technikerstraße 21A, A-6020 Innsbruck, Austria

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We investigate the emergence of subdiffusive transport by obstruction in continuum models for molecular crowding. While the underlying percolation transition for the accessible space displays universal behavior, the dynamic properties depend in a subtle nonuniversal way on the transport through narrow channels. At the same time, the different universality classes are robust with respect to introducing correlations in the obstacle matrix as we demonstrate for quenched hard-sphere liquids as underlying structures. Our results confirm that the microscopic dynamics can dominate the relaxational behavior even at long times, in striking contrast to glassy dynamics.

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Introduction.—The basic paradigm of complex transport in disordered structures was formulated originally by Lorentz [1] as the motion of a tracer particle in a random medium of independently distributed arrested scatterers. Besides being a testing ground of kinetic theory [2], the Lorentz model has found a fertile soil in many applications, for example, electrical conductivity due to impurity scattering [3], hydrogen storage in hierarchically structured porous materials [4], molecular sieving [5,6], flow in porous media [7,8], and also in connection to oil recovery [9]. A striking prediction is the emergence of subdiffusive motion, which generically occurs in the crowded world of biological cells [10–14]. Concomitantly, the model exhibits a localization transition [15–17], which has also been found in fluids confined to porous host structures [18–20], and, at intermediate time scales, also in nanoporous silica melts [21–23] or in size-disparate mixtures [24,25].

At the localization transition, the diffusion coefficient vanishes due to subdiffusive motion of the tracer on arbitrarily long time scales [15]. This dynamic transition is driven by a continuum percolation transition of the underlying geometry [16,17], sometimes called the Swiss cheese model. Upon increasing the excluded volume, the spanning cluster in the accessible space is diluted until, at a critical excluded volume fraction, it becomes self-similar with fractal dimension \(d_f \approx 2.53\) for space dimension \(d = 3\). Hopping transport on such fractals, coined the “ant in the labyrinth” by de Gennes for critically diluted lattices [26], is equivalent to the conductivity problem of percolating random resistor networks (RRNs) [27]. The mean-square displacement (MSD) of a tracer on the critical infinite cluster becomes itself self-similar, \(\delta r_{\infty}^2(t) \sim t^{2/d_w}\), where \(d_w\) is known as the walk dimension. In the vicinity of the transition, universal scaling laws are expected to hold [28–30], concomitant with a power-law growth of the correlation length as controlled by the exponent \(\nu \approx 0.88\) (\(d = 3\)) [28]. Field-theoretical renormalization group arguments explain that the scaling behavior does not depend on the microscopic details and is characterized by universal exponents. While for structural properties, lattice and continuum percolation belong to the same universality class [31], the dynamic universality class describing transport splits similarly to the celebrated models \(A – J\) for continuous phase transitions [32,33]. The reason is that, for continuum percolation, long-range transport depends on the passage through arbitrarily narrow channels. The transition rates \(\Gamma\) through the channels become power-law distributed, \(\varrho(\Gamma) \sim \Gamma^{-\alpha}\), for small \(\Gamma\). A renormalization group analysis shows that the narrow channels either become irrelevant upon coarse graining or dominate the critical transport entirely [34]. Explicitly, the walk dimension obeys the exponent relation

\[
d_w = \max\{d_w^{\text{lat}}, d_f + [\nu(1 - \alpha)]^{-1}\},
\]

where \(d_w^{\text{lat}}\) is the universal exponent for Boolean RRNs and for diffusion on lattices [28,35].

While in two dimensions the universality class of RRNs takes over [36], simulations for the 3D ballistic Lorentz model [16,37] confirm the importance of the narrow gaps. In particular, the prediction by Machta and Moore [38] for the exponent \(\alpha = 1 – (d – 1)^{-1}\) has been corroborated for both the motion on the infinite cluster and the motion averaged over all clusters.

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In this Letter, we investigate the robustness of the critical dynamics near the localization transition by relaxing some idealizations of the Lorentz model. First, we use quenched hard-sphere fluids as realistic host structures, replacing the uncorrelated overlapping spheres of the original model and thereby changing the statistics of channel widths for the tracer particle. Second, we gradually change the microscopic dynamics from ballistic to Brownian motion, which affects the transit through narrow channels in the system. 

*Model.*—We have equilibrated moderately dense hard-sphere configurations consisting of $(3–5) \times 10^6$ particles of diameter $\sigma_{\text{core}}$ at packing fractions $\eta = 0.1$ to $0.4$. Around each of the particle centers, we draw a sphere of diameter $\sigma > \sigma_{\text{core}}$ such that a pointlike tracer is confined to the remaining void space—the emerging structure is also known as the cherry-pit model [39]. The overlapping Lorentz model then corresponds to $\sigma_{\text{core}} = 0$, i.e., to vanishing packing fraction $\eta = 0$; see Fig. 1(a) for illustration. To ensure proper equilibration of the obstacle matrix, we have monitored the pair-distribution function and compared it to the Percus-Yevick approximation [40] [see Fig. 1(b)]. Furthermore, we have generated a jammed hard-sphere configuration with resulting packing fraction $\eta \approx 0.6438$ using the Lubachevsky-Stillinger algorithm [41,42].

Long-range transport in such quenched structures occurs only if the void space percolates through the entire system. In the following, we focus on the critical interaction distance $\sigma$ that marks the percolation transition. The threshold can be determined efficiently by a Voronoi tessellation of the obstacle centers [31]; edges of the tessellation closer than $\sigma$ to an obstacle center are removed. Upon increasing $\sigma$, more and more edges are removed up to the point where the residual network barely spans the simulation box [see Fig. 1(c)]. The percolation transition as a function of the packing fraction is discussed in the Supplemental Material [43].

The void space of the cherry-pit structures can be viewed as a network of pores connected by *channels*, where each channel corresponds to an edge of the diluted Voronoi tessellation. For each channel, we define the width $w$ as the distance $\sigma + w$ of its Voronoi edge to the closest obstacle center. Then $w$ corresponds to the radius of the largest sphere that fits through this particular channel—only channels with $w > 0$ can be passed by the tracer. At the percolation transition, the majority of channels is blocked and even the most likely channel width is inaccessible to the tracer (see Fig. 2). The distribution is single peaked for quenched hard-sphere liquids, and structural correlations become more pronounced upon increasing the packing fraction. Then the probability for narrow channels, $0 \leq w \ll \sigma$, increases by a factor of $\approx 2$; simultaneously, the distributions become broader and more uniform. The channels associated with the infinite cluster display similar variations. The jammed structure peaks at a minimal channel width corresponding to three particles at contact. Yet, at vanishing channel width, $w \approx 0$, the distribution shows again a regular variation.

*Probing structural correlations.*—We have monitored the motion of a single tracer particle exploring the void space by event-driven molecular dynamics simulations

![FIG. 1.](image)

(a) Transport of a tracer particle (diameter $\sigma_T$) in a quenched hard-sphere fluid (left) is mapped to the transport of a pointlike tracer in the cherry-pit model (right). Cherry-pit obstacles consist of a hard core of diameter $\sigma_{\text{core}}$ and a shell of width $\sigma - \sigma_{\text{core}}/2 = \sigma_T/2$. Shells of different obstacles can overlap, but the shells cannot be penetrated by the point tracer. (b) Pair-distribution function $g(r)$ for hard-sphere fluids at packing fractions $\eta = 0.10, 0.25, 0.40$ (the solid lines) compared to the Percus-Yevick approximation (the dotted lines). (c) Voronoi tessellation in the cherry-pit representation ($d = 2$ for illustration). The blue line indicates a path on the percolating cluster containing a narrow channel (the green line).

![FIG. 2.](image)

FIG. 2. Probability density of channel widths $w$ at the percolation threshold for different packing fractions $\eta$ of the quenched hard-sphere liquid and a jammed hard-sphere configuration. Full lines correspond to all channels, negative widths are inaccessible to the tracer. Dashed lines are the contribution of the spanning cluster. (Right inset) Illustration of a channel between three neighboring cherry pits. (Left inset) Relation between width $w$ and length $L_w \sim \sqrt{w/\sigma}$ of a narrow channel, depicted for the 2D case.
(see the Supplemental Material [43]). Our first set of results is for “ballistic” tracers undergoing specular reflections from the obstacles. The interaction distance $\sigma$ has always been tuned to the percolation threshold.

The MSDs for different packing fractions including the overlapping Lorentz model ($\eta = 0$) and jammed configurations are displayed in Fig. 3. The short-time ballistic motion crosses over smoothly to subdiffusive motion, $\delta r_\infty^2(t) \sim t^{2/d_w}$, extending over more than seven temporal decades. As a most sensitive test for the anomalous exponent, we have evaluated the local exponents $\gamma_\infty(t) = d\log \delta r_\infty^2(t)/d\log t$. Then the data extrapolate nicely (see Fig. 3) to the longtime limit $\gamma_\infty(t \to \infty) = 2/d_w$, with the same exponent $d_w = 4.81$ for all densities, which is the well-established value for the overlapping case [16,17].

Probing the microdynamics.—Second, we have varied the microdynamics of the tracer, starting with deterministic ballistic motion and specular reflections, and then gradually adding randomness. Thereby the narrow channels are probed differently, potentially modifying their respective “conductances.” Since structural correlations do not affect the value of $d_w$ as shown above, the simulations are performed only for the overlapping Lorentz model ($\eta = 0$). One possibility to introduce a source of randomness is by changing the scattering rule off the obstacles: In diffuse scattering the outgoing direction is random in the accessible hemisphere, keeping the magnitude of the velocity fixed, which models a roughness of the scatterer surfaces. Figure 4 reveals that this does not affect the longtime behavior within our time window.

Next, we consider pseudo-Brownian motion within a coarse-grained scheme where the ballistic trajectory is interrupted after fixed time intervals $\tau_B$ and a random velocity is assigned according to a Maxwell distribution [51]. Then Fig. 4 (see also the Supplemental Material [43]) demonstrates that for pseudo-Brownian motion the MSD grows faster and the walk dimension changes to $d_w = 4.24$.

The crossover from the ballistic universality class towards the Brownian one is sensitive to the algorithmic time scale $\tau_B$. A proper mimicry of Brownian motion requires $\tau_B$ to be chosen as small as possible, yet the integration step of the simulation becomes very small and hence computationally unfeasible. Relying on a larger $\tau_B$ is delusive since then the narrowest channels are probed ballistically rather than diffusively. In fact, increasing $\tau_B$ by factors of 10 and 100 yields an apparent convergence of the local exponents to values in between (data not shown).

Discussion.—To rationalize our findings, we reconsider the arguments [52,53] for the power-law tail $g(\Gamma) \sim \Gamma^{-\alpha}$ in the distribution $g(\Gamma)$ of small transition rates $\Gamma$. The probability density is connected via $g(\Gamma)d\Gamma = P(w)dw$ to the probability density of a narrow channel. Figure 2, however, shows that $P(w)$ is not singular for narrow channels and attains a finite value $P(w \to 0)$. This insight explains the robustness of the walk dimension with respect to introducing spatial correlations in the host structure.

Therefore, a change in the dynamic universality class must originate from the relation between the transition rate and the width of a channel. With each channel of width $w$ and transition rate $\Gamma$, we associate a “conductance” $g(w) = \Gamma/A_w$, respectively a “conductivity” $\sigma(w) = (\Gamma/A_w)L_w$, where $A_w$ is a typical cross-sectional area of a channel and $L_w$ its effective length. For narrow channels $A_w \sim w^{d-1}$, and narrow channels remain narrow on channel lengths $L_w$. From the inset of Fig. 2 one infers $(L_w/2)^2 + (\sigma - w/2)^2 = \sigma^2$, which yields $L_w \sim \sqrt{\sigma w}$ for small channel widths $w$.

For ballistic motion, a particle hitting a channel at the correct angle will pass through the channel like a pinball, irrespective of the length of the channel. Then one
Eq. (1) yields widths, $P_{RRN}$, transport, respectively, or to the conventional lattice translates to the universality class of ballistic and Brownian motion. Here and earlier [16,37].

In contrast, for Brownian particles it is the conductivity that is expected to become constant for small channel widths, $\sigma(w \to 0) = \text{const}$. Then the transition rates follow $\Gamma \sim \sigma(w \to 0) w^{d-1} L_{\text{lat}}^{-1}$, which yields $q(\Gamma) = P(w \to 0) dw/d\Gamma \sim \Gamma^{-(d-2)/(d-1)}$ for $\Gamma \to 0$, which yields $1 - \alpha = (d-1)^{-1}$ consistent with the prediction of Machta and Moore [52] and confirmed here and earlier [16,37].

The hopping rates between the cells can be measured in Lorentz model (\cite{43}). Here, we follow a different approach and randomly assign hopping rates between nodes connected by unblocked edges according to the following distributions: proportional to, first, the measured cross-sectional area $A_w$ and, second, the anticipated asymptotic behavior of the cross section $\propto w^2$. Third, we have employed hopping rates $\propto \sqrt{w^2}$ in accordance with the expected Brownian probing and, last, also hopping rates independent of the channel width as suggested from a lattice RRN. From the inset of Fig. 4, one infers that, indeed, the dynamic exponent changes with the microdynamics, and extrapolates to the universality class of ballistic and Brownian transport, respectively, or to the conventional lattice RRN, $d_w^{\text{lat}} = 3.88(3)$.

**Conclusion.**—We have presented high-precision simulation data for transport in Lorentz models including structural correlations and different microdynamics of the tracer. The exponents associated with the anomalous transport are robust with respect to correlations in the arrested host structure. Changing the dynamic rules from ballistic motion to Brownian motion yields a different universality class.

The sensitivity of the asymptotic dynamics on microscopic details is in remarkable contradiction to the dynamic behavior of a glass-forming system close to structural arrest. There one of the hallmarks is that molecular glass-forming liquids with Newtonian dynamics behave identically to colloidal suspensions with Brownian or overdamped dynamics [54–56]. Intuition suggests that the slow dynamics occurs in a rough free energy landscape provided by the configuration rather than phase space, such that ballistic and Brownian dynamics should behave identically. This picture is justified by the escape of a particle from its cage being a local phenomenon even after coarse graining. In contrast, the slow dynamics on the emergent fractal structure close to the percolation transition is driven by a divergent length scale and the renormalization flow amplifies the role of narrow channels upon coarse graining.

Evidence for the robustness of the universality class with respect to structural correlations has been collected earlier [57], e.g., by introducing polydisperse obstacles [58]. However, there the simulation was for 2D systems, where the exponent relation equation (1) yields $d_w = d_w^{\text{lat}}$ anyway. Similarly, a recent experimental realization [8] of the cherry-pit Lorentz model in $d = 2$ combined with a simulation for soft spheres showed compatibility with the lattice value for $d_w$. In $d = 3$, structural correlations were investigated before [59] with the same conclusion that the exponent $d_w$ is robust, yet for dissipative particle dynamics (DPD) and with significantly lower statistical accuracy.

Our data for Brownian motion are the first confirmation of the splitting of the dynamic universality class in Lorentz models. Note that the standard algorithm to generate Brownian motion [51] is specious since the scale-free motion is replaced by a different microdynamics at small scales. Yet, narrow channels dominate transport at the percolation threshold and, correspondingly, the narrowest channels are always probed incorrectly. This explains why it has been inferred earlier [17] that (pseudo-)Brownian motion would yield critical exponents identical to the ballistic case. Presumably, the same discrepancy is present in Ref. [59].

That the underlying dynamics may be relevant for anomalous transport is anticipated from the wider perspective [10–14]. For example, in the Lévy-Lorentz gas [60,61] a tracer collides with a diluted fractal structure, resulting in anomalous superdiffusion for ballistic dynamics, while Brownian tracers display ordinary diffusion. Second, the single-file diffusion along 1D channels [62–64] becomes subdiffusive for Brownian dynamics, whereas normal diffusion results for ballistic particle motion. The Lorentz model differs from these examples since the underlying percolation transition constitutes a static critical phenomenon with universal exponents. Different values of the walk dimension $d_w$ for different microscopic dynamics imply a paradigm-breaking splitting of the universality class.

It is interesting to ask whether even more dynamic universality classes exist. For example, if the colloidal realization of the Lorentz model by Skinner et al. [8] could be done in $d = 3$, one expects that hydrodynamic effects due to thin lubrication layers dominate transport through the narrowest channels. Similarly, in the complementary molecular dynamics simulations [46], the percolation threshold is set by the energy of the tracer such that the
narrow channels are the ones where the energy barely suffices to pass the barriers. Then, by the bottleneck effect, the time to pass these barriers becomes long, giving rise to a singular energy dependence of the conductivity.

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"Corresponding author.
thomas.franosch@uibk.ac.at


