Crossover in the Slow Decay of Dynamic Correlations in the Lorentz Model

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The long-time behavior of transport coefficients in a model for spatially heterogeneous media in two and three dimensions is investigated by Molecular Dynamics simulations. The behavior of the velocity auto-correlation function is rationalized in terms of a competition of the critical relaxation due to the underlying percolation transition and the hydrodynamic power-law anomalies. In two dimensions and in the absence of a diffusive mode, another power law anomaly due to trapping is found with an exponent \(-3\) instead of \(-2\). Further, the logarithmic divergence of the Burnett coefficient is corroborated in the dilute limit; at finite density, however, it is dominated by stronger divergences.

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Spatial heterogeneities often give rise to intriguing slow dynamics in complex materials, manifested for example by broad frequency-dependent relaxation processes in colloidal gels which form stress-sustaining networks close to the sol-gel transition \([1,2,3]\). Similarly, the presence of differently sized proteins, lipids and sugars in the cytoplasm of eukaryotes, summarized as cellular crowding, is identified by slow anomalous transport as its most distinctive fingerprint \([4,5,6]\).

For the Lorentz model itself, there is a long-standing disagreement between analytic theory and simulations about the freezing transition \([9]\). At intermediate time scales, a regime of particles in their cages \([10]\). The long-time behavior exhibits an intriguing cross-over scenario from long-living positive correlations, \(\psi(t) \simeq \Delta t^{-3/2}\), to a high-density regime characterized by slowly decaying anti-correlations, \(\psi(t) \simeq -\Delta t^{-5/2}\). The former corresponds to the celebrated long-time anomaly in simple liquids \([11]\), connected to the formation of a vortex pattern due to local momentum conservation. The mechanism for the latter decay is presumably of totally different origin: in an array of immobilized obstacles, the dynamics of a tagged particle always remembers its frozen cage—a mechanism well-known for the Lorentz model \([8]\).

For the Lorentz model itself, there is a long-standing discrepancy between analytic theory and simulations about the manifestation of the long-time tail. The existence of the long-time anomaly in the Lorentz model has been predicted within a rigorous low-density expansion as \(\psi(t) \simeq -\Delta t^{-d/2-1}\) for \(t \rightarrow \infty\) \([12,13]\). Earlier computer simulations on two-dimensional systems \([14,15,16]\) identified a long-time relaxation of power-law type. At low densities, the expected exponent was confirmed; the amplitude, however, differed significantly from the theoretical prediction. At intermediate densities, the simulation results again suggest power-law behavior, which was described phenomenologically by non-universal, density-dependent exponents \([15,17]\).

The regime of higher obstacle densities poses considerable challenges for theory; sequences of repeated ring collisions have been accounted for by a self-consistent variational repeated-ring theory \([18]\). Götze et al. \([19]\) have developed a mathematically consistent theory that covers the physics of the low-density regime up to the predicted localization transition. In particular, they predict a competition between a critical power-law relaxation due to the fractal clusters at the percolation transition and the universal long-time tail. A similar scenario has been proposed for lattice variants of the Lorentz model \([20]\), and there, evidence for a cross-over scenario has been reported \([21]\).

In this Letter, we present high-precision data for the two-dimensional overlapping Lorentz model for reduced obstacle densities, \(n^* := n \sigma^d\), ranging from the dilute gas, \(n^* = 0.005\), up to the percolation threshold, \(n^*_c \approx 0.35907\) \([22]\), and deep into the localized phase. In particular, we focus on the algebraic decay of the VACF at long times which is predicted for asymptotically low densities in dimensionless units as \([13]\)

\[
\psi(s) \simeq -\frac{n^*}{\pi} \frac{1}{s^2} \quad \text{for} \quad s \rightarrow \infty, \quad n^* \rightarrow 0, \quad d = 2,
\]

where \(s = t/\tau\) is the mean number of collisions and \(\tau^{-1} = 2n^*v/\sigma\) the collision rate \([22]\), and \(v\) denotes the velocity of the particle. In order to observe the universal tails, we analyze \(\psi(t)\) up to times corresponding to several \(10^4\) collisions, which implies that a noise level in the correlation of the order of \(10^{-8}!\) is required. Relying on an event-oriented algorithm, we have simulated some \(10^6\) trajectories per obstacle density, each trajectory covering \(10^6\) to \(10^8\) collisions. We have calculated \(\psi(t)\) by directly correlating velocities and obtain accurate data up to a noise level of \(10^{-5}\). Furthermore, we have measured the mean-square displacement (MSD), \(\delta r^2(t) := \langle \Delta \mathbf{R}^2(t) \rangle\), and extracted the diffusion coefficient \(D\) from \(\delta r^2(t \rightarrow \infty) \simeq 4Dt\). An alternat-
tive route to evaluate $\psi(t)$ is to perform a numerical second derivative of $\delta(t)^2$. We have checked that both methods yield identical results within statistical errors. The second method further suppresses the noise level by several orders of magnitude, up to a factor $10^3$. No smoothening or sophisticated data manipulation has been used to obtain the derivatives.

Results for the VACF are shown in Fig. 1 for the full density range in the diffusive phase. On linear scales, the data for the lowest density are indistinguishable from the exponential relaxation $\exp(-4t/3\tau)$ of the Lorentz-Boltzmann theory. For intermediate densities ($n^* \gtrsim 0.1$), the VACF enters the region of anti-correlation already after two collisions. Since the diffusion coefficient is related to the total area under the VACF by a Green-Kubo relation, $D = (v^2/\langle d \rangle) \int_0^\infty \psi(t) dt$, the areas of positive and negative region cancel exactly at densities equal and above the percolation threshold, $n^*_c$. In a double-logarithmic representation, the data corroborate power-law behavior for time windows covering 1–2 decades or, equivalently, 2–4 decades in correlations. A gradual increase of the density towards $n^*_c$ gives rise to apparent density-dependent exponents, at least if correlations below $10^{-4}$ are ignored. Careful inspection of the VACF for $n^* = 0.20$ reveals an intermediate power-law regime as well as an universal long-time tail, consistent with the competition of critical and universal relaxation predicted by Götze et al. [19].

As a most sensitive test for the crossover scenario, Fig. 2 exhibits the VACF multiplied by the expected power law $s^2$ of the universal tail. One infers that $s^2\psi(s)$ saturates at a constant in the accessible time window for densities up to about $2/3$ of the percolation threshold, $n^* \lesssim 0.25$. For densities $n^*_c \lesssim 0.1$, the constant is approached from above in qualitative agreement with the prediction of Das and Ernst [23] for the sub-leading long-time behavior,

$$\psi(s) \simeq -(n^*/\pi s^2) \{1 + 63/16s + \ldots\}. \tag{2}$$

For higher densities, one observes an increase, following an apparent density-dependent power law, before the universal tail is attained. The time scale where the crossover occurs shifts to longer times as the percolation threshold is approached, confirming the predicted scenario [19]. The density $n^* = 0.10$ reaches its asymptotic value remarkably early; this is due to a cancellation effect of the sub-leading universal tail and the onset of critical slowing down.

Very close to $n^*_c$, the VACF exhibits the critical relaxation $\psi(t) \sim t^{2/z-2}$, which follows directly from the prediction for the MSD, $\delta(t)^2 \sim t^{2/z}$. The numerical value of the exponent, $z \approx 3.03$ [33], coincides with results of simulations for diffusion on lattice percolation [24], corroborating that the transport properties of the Lorentz model in the close vicinity of the transition share the same universality class [34].

Long-time tails originating from power-law distributed exit rates of the cul-de-sacs have been predicted even in the localized regime [27, 28], i.e., for obstacle densities above $n^*_c$. In particular, the VACF should then decay as $\psi(t) \sim t^{-3}$ for $n^*_c > n^*_c$ and $d = 2$; a prediction that has not been tested so far. Appropriate rectification plots are included in Fig. 2 and one infers that the data follow such a power law for one order of magnitude in time, i.e., three decades in correlation.

We have extracted dimensionless amplitudes $A$ of the universal tail as the long-time limit of $-s^2\psi(s)$. In the regime of intermediate densities, our data are in semi-quantitative agree-
ment with earlier simulations \cite{16,17}, see Fig. 3. As has been observed before, the values of $A_0$ are significantly larger than the low-density prediction, $A_0 = n^*/\pi$. Since the calculation of $A_0$ relies on a perturbative correction to the Boltzmann-Lorentz equation \cite{13}, quantitative agreement requires the diffusion coefficient $D$ to be sufficiently close to the Boltzmann value $D_0 = 3\sigma/v_0 n^*$. As can be inferred from Fig. 3 this criterion is not met even at low densities; a 40\% suppression of $D/D_0$ occurs at $n^* = 0.10$, signalling the onset of sub-diffusive motion. The diffusion coefficient for $n^* \leq 0.01$ is in agreement with the first non-analytic correction of the low-density expansion \cite{12,14}

$$D_0/D = 1 - \frac{4n^*}{3} \ln n^* - 0.8775 n^* + 4.519 \left(n^* \ln n^*\right)^2. \quad (3)$$

Although the amplitudes $A$ appear to approach the low-density prediction as $n^* \to 0$, the value for $A$ at $n^* = 0.005$ still deviates by approximately 25\%.

Close to the percolation threshold, the crossover scenario suggests that the amplitude should actually diverge. Matching the critical relaxation, $\psi(t) \sim t^{2/\beta-2}$, and the universal tail $\psi(t) \sim -A(t/\tau)^{-3}$, at the divergent crossover time scale $t_\tau$ yields $\tau^2 A \sim t_\tau^{2/\beta}$. Assuming that $t_\tau$ also describes the crossover of the MSD from anomalous to diffusive transport, $t_\tau^{2/\beta} \sim Dt_\tau$, entails the prediction,

$$\tau^2 A \sim D^{-2/(\beta-2)} \sim |n^* - n^*_c|^{-(2\nu-\beta)} \quad (4)$$
as $n^* \to n^*_c$, where $\beta$ and $\nu$ are percolation exponents \cite{33}. The rapid increase of the amplitudes follows this prediction remarkably well; even at $n^* = 0.1$, Eq. (4) deviates by less than 30\% from the simulation results, whereas the low-density prediction is off by a factor 6, see Fig. 3.

The VACF or, equivalently, the MSD is only the simplest quantity exhibiting anomalous long-time behavior. Deviations from Fickian diffusion are indicated by a non-vanishing (super-)Burnett coefficient, which reads in two dimensions

$$B(t) = \frac{1}{4!} \frac{d}{dt} \left[ \frac{1}{2} \left( \Delta R(t) - \langle \Delta R(t)^2 \rangle \right) \right]. \quad (5)$$

Within a hydrodynamic mode-coupling approach, it has been predicted that the Burnett coefficient diverges logarithmically in $d = 2 \ll 37,28,29$. Indeed, $dB(t)/d\log(t)$ saturates at a constant for low densities, see Fig. 4. Again close to $n^*_c$, one expects this behavior to be masked by the critical relaxation. Dynamic scaling predicts a power-law divergence of the mean-quartic displacement, $\langle \Delta R(t)^4 \rangle \sim t^{4/z}$, where $z = (2\nu - \beta + \mu)/(\nu - \beta/4) \approx 2.95 < z \ll 25$. Then, the $B(t)$ increases according to $B(t) \sim t^{4/z-1}$ at the critical density—consistent with Fig. 4. The presence of finite clusters renders the dynamics spatially heterogeneous, even below $n^*_c$. A heterogeneous superposition of Gaussian processes yields a linearly divergent Burnett coefficient, $B(t) \approx \tilde{\alpha}_2 D^2 t$ for $t \to \infty$, with $\tilde{\alpha}_2 = (4/3)(1/P_{\infty} - 1)$, and $P_{\infty}$ denotes the fraction of mobile particles. We find semi-quantitative agreement with this prediction, see Fig. 4. In the dilute limit, the prefactor is expected to vanish as $\tilde{\alpha}_2 D^2 \sim n^*$. Let us briefly comment on the the long-time behavior of the VACF for the three-dimensional Lorentz model. Recently, the critical properties of the localization transition have been analyzed in terms of a scaling Ansatz for the van Hove correlation function \cite{25}. The exponent of the universal tail is larger,
an intermediate time window, time scales for momentum relaxation are taken by long-lived cages in the high-density regime. Hence, the negative tail, $\psi(s) \sim s^{-3/2}$, to the universal long-time tail, $\psi(s) \sim s^{-5/2}$, can be observed.

and the amplitude depends even stronger on the density

$$\psi(s) \sim -\frac{(3\pi)^{3/2}}{16} (n^*)^2 s^{-5/2} \quad \text{for } d = 3$$

where $s = t/\tau$ again, and the collision rate is given by $\tau^{-1} = \pi n^* v/\sigma$ for $d = 3$. Such a predicted behavior is much more difficult to observe, and to the best of our knowledge, only rudimentary evidence has been reported for the existence of this phenomenon \[13\]. Our results (Fig. 5) suggest a similar crossover scenario as for $d = 2$: the universal long-time tail with exponent $-5/2$ is preceded by a critical relaxation with exponent $2/3 - 2 \approx -1.68$; the latter covers a growing time window upon approaching the localization transition.

Finally, we emphasize again the universality of the negative tail: it relies on the general mechanism that the particle can return in its frozen heterogeneous environment by reversing its path, thus remembering the presence of free volume \[8\]. For the hard-sphere fluid of Ref. \[9\], the role of the frozen environment is taken by long-lived cages in the high-density regime. Hence, the negative tail, $\psi(t) \simeq -A_0 t^{-5/2}$, should emerge in an intermediate time window, $\tau \ll t \ll \tau_\alpha$, bounded by the time scales for momentum relaxation $\tau$ and structural relaxation $\tau_\alpha$; the slowing down of the latter is also reflected in a rapid increase of the viscosity of the fluid, $\eta \sim \tau_\alpha$. At even larger times, the positive hydrodynamic tail, $\psi(t) \simeq A_\theta t^{-3/2}$, is expected to follow although its amplitude should vanish rapidly, $A_\theta \sim \eta^{-3/2}$ \[11\].

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[1] A. D. Dinsmore, V. Prasad, I. Y. Wong, and D. A. Weitz, Phys. Rev. Lett. 96, 185502 (2006).
nificant corrections to scaling decaying even slower than in the three-dimensional case [25, 26].