Solid-like mean-square displacement in glass-forming liquids

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It was recently shown [S. P. Bierwirth *et al.*, Phys. Rev. Lett. **119**, 248001 (2017)] that the real part of the frequency-dependent fluidity for nine glass-forming liquids of different chemistry conforms to the zero-shape-parameter prediction of the Random Barrier Model for ac electrical conduction in disordered solids. This surprising finding can be explained by the frequency-dependent fluidity being proportional to the frequency-dependent diffusion coefficient and the mean-square displacement being well described by the Random Barrier Model. We present data from extensive GPU based molecular dynamics simulations of a crystallization-resistant modification of the Kob-Andersen binary Lennard-Jones mixture confirming this picture. This emphasizes the challenge of explaining why a simple model based on hopping of non-interacting particles in a fixed random energy landscape can reproduce the complex and highly cooperative dynamics of glass-forming liquids. Our data indicate, tentatively, that an understanding of this should refer to the high-dimensional configuration space, not 3d space.

Gainaru and coworkers recently demonstrated from experimental data for nine glass-forming liquids a striking universality of the real part of the frequency-dependent fluidity [1]. The fluidity is defined as $F(\omega) \equiv 1/\eta(\omega)$ in which ω is the angular frequency and $\eta(\omega)$ the complex frequency-dependent linear shear viscosity. The data analyzed involved van der Waals, ionic, and hydrogen-bonding liquids, i.e., chemically quite diverse systems. The universal fluidity data were shown to fit well to the prediction of the random barrier model (RBM). This is highly non-trivial, given the fact that the model has no shape parameters and was devised for describing ac hopping conductivity in disordered solids, not viscous liquid dynamics[2, 3].

The relaxation time increases dramatically when a liquid is supercooled and approaches the glass transition [4–8]. A standard probe of the dynamics is the single-particle mean-square displacement (MSD) as a function of time, $\langle \Delta r^2(t) \rangle$, in which $\Delta r(t)$ is the distance traveled by a given atom or molecule in time t and the angular brackets denote an ensemble average. At long times, the MSD is proportional to time and determines the (self) diffusion coefficient D via $\langle \Delta r^2(t) \rangle = 6Dt$ $(t \to \infty)$. The transition to linear-time MSD takes place roughly at the time where the particles on average has moved an interatomic distance. Times shorter than this define the so-called subdiffusive regime. Since all liquids become diffusive at long times, it is the subdiffusive regime that contains information about the nature of the liquid dynamics.

The RBM was devised as an idealized model of ac ionic or electronic hopping conduction in disordered solids like oxide glasses, polymers, amorphous semiconductors, etc [2]. The model considers non-interacting particles jumping stochastically on a simple cubic lattice with identical site energies and random energy barriers for nearest-neighbor jumps. In the extreme-disorder limit, i.e., when k_BT is much smaller than the relevant energy barriers, the RBM predicts a universal zero-shape-parameter MSD, i.e., the MSD is the same for all barrier distributions except for scaling of time and space [3]. This is because the dynamics at extreme disorder is dominated by percolation in the 3d random energy landscape [3].

The frequency-dependent diffusion coefficient of the RBM, $D(\omega)$, is predicted in a simple analytical approximation to be the solution of $\ln \tilde{D} = (i\tilde{\omega}/\tilde{D})^{2/3}$ in which $\tilde{\omega}$ is a properly scaled frequency and $\tilde{D} \equiv D(\omega)/D(0)$ [9]. This is derived by combining the Alexander-Orbach conjecture that the percolation cluster independent of dimension has harmonic dimension 4/3 [10] with the effective medium approximation applied to diffusion on the percolation cluster [9]. The quoted equation provides an excellent fit to computer simulations of the RBM [9] except at the lowest frequencies where the transition to frequency-independent diffusion constant is better described by the solution to the following modified equation $\ln \tilde{D} = (i\tilde{\omega}/\tilde{D})(1 + (8/3)i\tilde{\omega}/\tilde{D})^{-1/3}$.[9] This reflects the fact that the percolating cluster above the transition becomes homogeneous on long length-scales.

If the RBM describes the liquid MSD and if one assumes that the macroscopic shear viscosity controls the microscopic frictional forces via the Stokes-Einstein relation, the frequency-dependent fluidity is proportional to the RBM universal prediction, as found for nine liquids by Gainaru and coworkers [1]. The findings of Ref. 1 give rise to two questions, however: 1) How can one justify using the Stokes-Einstein relation between diffusion coefficient and viscosity, given the fact it generally breaks down for glass-forming liquids [6, 11–14]? 2) How can a model based on non-interacting particles jumping in a fixed energy landscape provide a realistic picture of highly cooperative liquid dynamics? This paper aims at providing a step toward answering the second question. This is done by extensive molecular dynamics simula-

tions of a model glass former. The idea is that if there is a universal viscous-liquid dynamic fluidity described by the RBM, this should be observed also in computer simulations. We do not discuss the Stokes-Einstein question, but note that for the arguments presented it is enough that the frequency-dependent viscosity and diffusivity are inversely proportional – the proportionality coefficient may change with state point.

MSD data of simulations are conveniently fitted to the von Schweidler empirical expression [15]

$$\langle \Delta r^2(t) \rangle \;=\; r_0^2 \;+\; a(6Dt)^b \;+\; 6Dt\,. \qquad (1)$$

According to mode-coupling theory, the exponent b is non-universal [16]. Tokuyama has discussed common features of the MSD of different models [17], but to the best or our knowledge the possibility of a universal MSD has not been considered in the literature. This means that the glass community after the publication of Ref. 1 finds itself in the unusual situation that experiments suggest a *more* universal behavior than reported in simulations. An important difference between experiments and simulations, however, is that the latter cannot yet cover the long time scales characterizing experiments on highly viscous liquids. Is this why the MSDs reported in simulations, though similar, are not universal? To address this question one needs a viscous model liquid that is fast and easy to simulate and which does not crystallize, even in very long simulations. Recent exciting developments with swap dynamics have made it possible to generate equilibrium states of liquids with extremely long relaxation times [18, 19], but probing the alpha relaxation dynamics on these time scales remains out of reach. Brute-force molecular dynamics (MD) is still the only available option – here we utilize state-of-art GPU simulations [20] to access equilibrium dynamics at very low temperatures. The duration of the longest simulation was four months, which with traditional CPU computing would have taken several years.

For almost a century the standard model in liquid-state theory has been the Lennard-Jones (LJ) system based on the following pair potential in which ε is a characteristic energy and σ a characteristic length: $v(r) = 4\varepsilon\left[(r/\sigma)^{-12} - (r/\sigma)^{-6}\right]$ [21, 22]. The LJ liquid cannot be studied in the supercooled phase where it readily crystallizes. In 1995 Kob and Andersen proposed a binary LJ system that is easily supercooled. The Kob-Andersen (KA) model is a mixture of 80% large A particles and 20% small B particles [23]. The trick is to have a strong AB non-ideal (non-Lorentz-Berthelot) attraction impeding phase separation; the parameters of the KA model are [23] $\sigma_{BB}/\sigma_{AA} = 0.88$, $\sigma_{AB}/\sigma_{AA} = 0.8$, $\varepsilon_{BB}/\sigma_{AA} = 1.5$, and $\varepsilon_{BB}/\varepsilon_{AA} = 0.5$.

The KA model quickly became the standard model for simulations of viscous liquid dynamics [24]. The mode-coupling temperature – the temperature at which idealized mode-coupling theory based on higher-temperature data predicts a diverging relaxation time [19] – was estimated to be $T_c = 0.435$ [23]. As computers became faster, it eventually became possible to investigate the model below $T_c = 0.435$, see eg. Refs. 24 and 25. The KA model *does* crystallize in very lengthy simulations [26, 27]; in fact, at the standard density 1.20 the KA liquid is supercooled whenever $T < T_m = 1.03$. [28]. Although the strong AB attraction impedes phase separation, the supercooled KA system eventually does crystallize by phase separating into a pure A phase.

Is it possible to modify the KA model to make it even

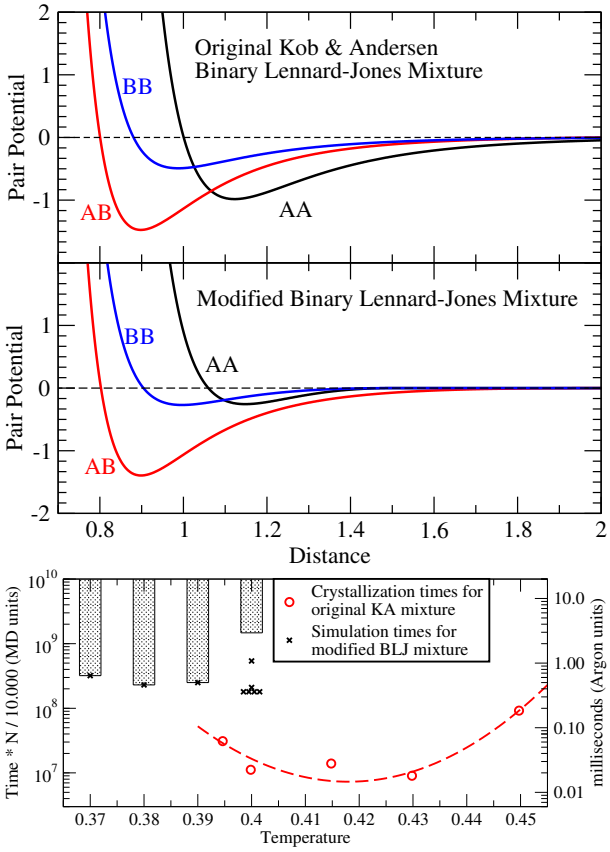

FIG. 1. (a) Pair potentials in units of ε_{AA} as a function of pair distance in units of σ_{AA}. The upper panel shows the Kob-Andersen (KA) binary Lennard-Jones pair potentials. The lower panel shows the modified binary Lennard-Jones (mBLJ) pair potentials, which introduce shifted-force cutoffs at $r = 1.5\,\sigma_{AA}$ for the like-particle interactions, thereby suppressing the tendency of phase separation. (b) The red circles give the average crystallization times of the KA model [27], the dashed red curve is a parabolic best fit to these data. The figure also shows the simulation times for the mBLJ model at four temperatures: $T = 0.37$; 0.38; 0.39; 0.40 (black crosses). Simulation times are scaled to be compared to the crystallization times of Ref. 27, which used N=10.000. At $T = 0.40$ several independent simulations were performed. At each temperature the black rectangles indicate the estimated range of possible crystallization times for the mBLJ model.

less prone to crystallization? We do this by introducing a shifted-force cutoff at $r = 1.5\,\sigma_{\rm AA}$ for the AA and BB interactions [29, 30], keeping the AB interaction as in the original model. Figure 1(a) shows in the upper panel the KA pair potentials and in the lower panel the modified binary Lennard-Jones (mBLJ) pair potentials. The AA attraction is here visibly weaker, and the BB attraction has also been weakened. The motivation for using a shifted-force cutoff was that this is known to leave the liquid dynamics almost unchanged [30], thus facilitating comparison between the original and the modified model.

We performed molecular dynamics simulations in the NVT ensemble with $N = 8000$ particles (unless otherwise noted), the "standard" number density $\rho \equiv N/V = 1.20$, and temperature T controlled by a Nose-Hoover thermostat. Unless otherwise noted results are reported in the standard MD-units, with $\sigma_{AA} = 1$, $\epsilon_{AA} = 1$, $m_A = m_B = 1$, and $k_B = 1$. The time-step was 0.005.

The mBLJ liquid did not crystallize during the months of GPU simulations performed for this study. Figure 1(b) shows as a function of temperature the average crystallization time of the original KA model (red circles) [27], and our total simulation times for the mBLJ system (black crosses). Since the mBLJ system did not crystallize, the simulation time gives a lower bound on the crystallization time; the black rectangles indicate where the unknown crystallization times are expected to be found. At $T = 0.40$ several independent simulations were performed. This includes simulations that were first equilibrated at the lower temperatures (0.37, 0.38, and 0.39, respectively), a procedure that is known to increase the tendency to crystallize. Based on the data presented, we estimate that the mBLJ liquid has at least a 100 times longer crystallization time than the original KA liquid.

Having modified the original KA model such that crystallization is in practice avoided, we turn our attention to the supercooled liquid dynamics. Figure 2 shows the mBLJ liquid's all-particle MSD as a function of time at four temperatures. The figure presents data going to times larger than 10^8 MD time units, corresponding to 0.2 milliseconds in argon units. The data are for $N = 8000$ particles; size independence was checked by simulating also $N = 27000$ particles at $T = 0.40$, which gave indistinguishable results. The dashed blue line gives data for the KA model at $T = 0.40$, which are close to those of the mBLJ model (blue crosses), confirming that the two models have very similar liquid dynamics.

At very short times one finds the well-known free-particle ballistic MSD $\propto t^2$ after which there is a plateau where the MSD is virtually constant. This derives from the "cage rattling" of the particles in local potential-energy minima, reflecting the fact that a viscous liquid over short time scales is virtually indistinguishable from an amorphous solid. At longer times the MSD increases, of course, and eventually one finds the standard diffusive behavior MSD $\propto t$. Note the dramatic slowing down

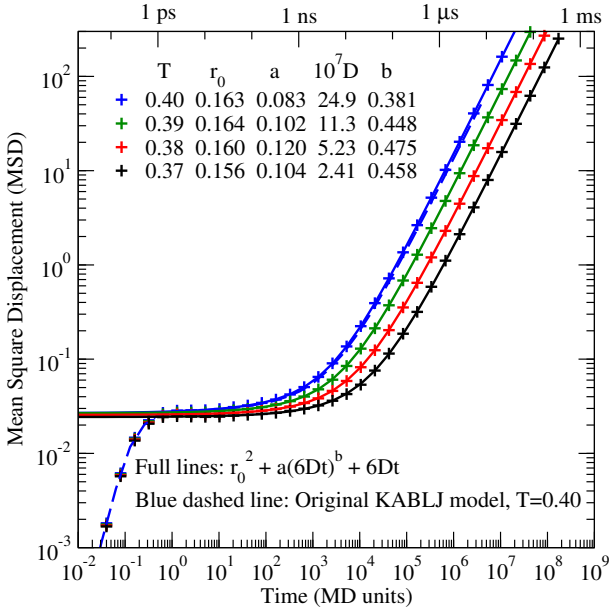

FIG. 2. All-particle MSD as a function of time for the mBLJ system at the four temperatures $T = 0.37$; 0.38; 0.39; 0.40. Full lines are best fit to the von Schweidler expression Eq. (1) [15]. The liquid dynamics of the mBLJ model is close to that of the KA mode; this is illustrated by the dashed blue line giving the MSD of the KA model at $T = 0.40$.

upon cooling: a temperature decrease of 7.5% results in more than one decade's slowing down. What causes this is, in a nutshell, the mystery of the glass transition [7, 8]. The full curves in Fig. 2 are fits to the von Schweidler expression Eq. (1) that works excellently.

Figure 3 investigate whether the MSD data exhibit time-temperature superposition (TTS), i.e., whether data collapse can be achieved by scaling of the axes, as found in experiment [1]. In their original paper Kob and Andersen found TTS by scaling time by the diffusion coefficient. In Fig. 3(a) we apply the same scaling to our low temperature MSD data, finding as expected a collapse in the diffusive regime (see inset). While there is also a good collapse in the transition to the diffusion regime, differences are found at shorter times in the plateau regime. In Fig. 3(b) we perform a further scaling on both axes by a parameter c, which has dimension of a squared length, thus making both axes dimensionless. The determination of the scaling parameter c is described below in connection with Fig. 4. From Fig. 3(b) one concludes that TTS applies very well.

Next we compare our low-temperature MSD data to the RBM prediction (Fig. 4). Full lines are the MSD scaled as in Fig. 2, including now also the ballistic regime. The RBM relates to spatially discrete particle jumps, so the predicted MSD does not include the short-time "cage-rattling" plateau observed in any realistic viscous liquid model. Consequently, to compare the RBM directly to the MSD data we add a constant reflecting the cage-

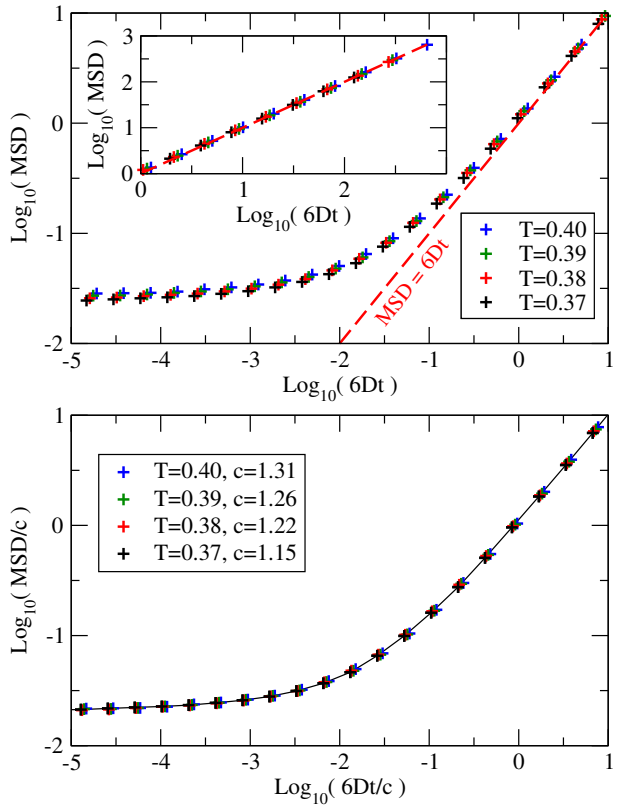

FIG. 3. (a) MSD at the four temperatures plotted as a function of time scaled by the diffusion coefficient D, showing data corresponding to $t > 20$ in MD units. The data superpose nicely, not just at long times but also in the transition region. However, the short-time "plateau" regions changes with temperature. The inset shows results for longer times, demonstrating that the diffusive behavior is given by the red dashed curve. (b) Same data as in a), but now scaled further on both axes by a squared empirical length c, showing a near-perfect collapse, i.e., time-temperature superposition. The black line is the von Schweidler fit to the the $T = 0.40$ data.

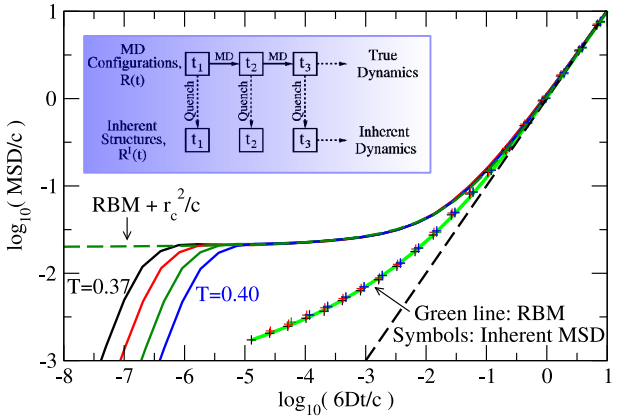

FIG. 4. MSD of true (full lines) and inherent dynamics (plus-symbols) compared to the RBM prediction, Eq. (2) and Eq. (3) respectively. The fit parameters were determined as described in the text. The agreement for both the true and the inherent dynamics demonstrates that the RBM, despite having no shape parameters, provides a good representation of the numerical data.

rattling contribution to the MSD. If the universal RBM prediction for the MSD corresponding to unit diffusion coefficient is denoted by $F_{\rm RBM}(t)$, the RBM prediction becomes:

$$\langle \Delta r^2(t) \rangle = c\, F_{\rm RBM}(\alpha t) \,+\, \beta \qquad (2)$$

with three parameters c, α, β. The long-time limit $\langle \Delta r^2(t) \rangle = 6Dt$ results in $c\alpha = D$, leaving two parameters. For dimensional reasons, there must be at least two fit parameters, a length and a time parameter. Eq. (2) is plotted as the green dashed line in Fig. 4. We conclude that Eq. (2) fits the MSD data very well, despite having only one shape parameter compared to the two shape parameters of the von Schweidler expression (Eq. (1)).

In the following we show that we can go one step further and compare the RBM model to the dynamics of the mBLJ model using just the two trivial scaling parameters, D and c, i.e., without any shape parameters. Already in 1969 Goldstein recognized the significance of potential-energy minima [31], later termed "inherent states" by Stillinger and Weber [32]. If the N particle coordinates are collected into a single $3N$-dimensional vector denoted by $\mathbf{R}$, one can distinguish between the "true" Newtonian dynamics $\mathbf{R}(t)$ and its corresponding quenched "inherent" dynamics $\mathbf{R}_{\rm I}(t)$. As illustrated in the inset of Fig. 4 the latter is arrived at by quenching configurations from an equilibrium MD simulation to their inherent states [33]. We run the same data analysis program on both the true configurations $\mathbf{R}(t)$ and the quenched inherent configurations $\mathbf{R}_{\rm I}(t)$. Note that $\mathbf{R}_{\rm I}(t)$ in the course of time jumps discontinuously from one constant vector to another. Below T_c the dynamics separates into oscillations around inherent states and transitions between these [33], as predicted by Goldstein [31]; in the inherent dynamics the effect of oscillations is removed. We refer to the inherent MSD as $\langle \Delta r_I^2(t) \rangle$. It is this quantity that should be compared directly to the RBM prediction without any additional constants:

$$\langle \Delta r_I^2(t) \rangle = c\, F_{\rm RBM}(\alpha t) \qquad (3)$$

In Fig. 4 the inherent MSD is plotted as crosses and is seen to exhibit TTS. The RBM prediction, Eq. (3) (full green line), agrees nicely with the data, despite having no shape parameters.

In the above analysis, the scaling parameter c was determined by minimizing the root-mean-square difference between the *inherent* MSD and the RBM prediction (Eq. (3)). Subsequently the plateau parameter β was fitted for the true MSD (Eq. (2)). The true MSD can be fitted directly to Eq. (2), but using the resulting c parameters for the inherent MSD results in a considerable worse fit. This reflects the fact that the inherent contri-

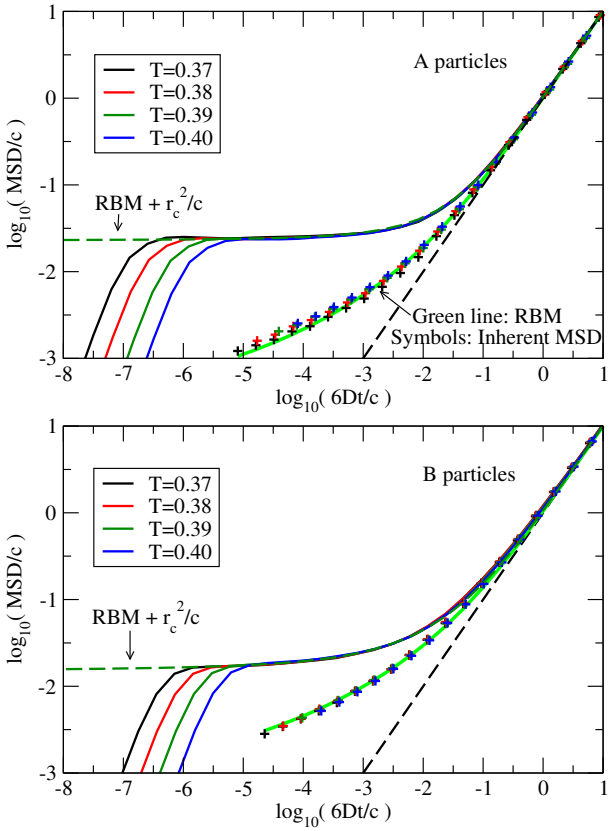

FIG. 5. Testing the RBM separately for each particle species with (a) showing the A particle MSD versus the RBM prediction and (b) showing the same for the B particles.

bution to the MSD is quite small at short times. Note, however, that the inherent MSD at short times is more than a factor 100 *larger* than the extrapolation of the diffusive regime (black dashed line) – this is comparable to the increase in fluidity observed in experimental data [1].

Why was the plateau parameter β not necessary in the analysis of experimental data in Ref. 1? Letting tilde denote suitable scaling, we get from Eq. (2):

$$\tilde{F}(\tilde{\omega}) = \tilde{F}_{\rm RBM}(\tilde{\omega}) + i\tilde{\omega}\beta \qquad (4)$$

For the real part of the fluidity as investigated in Ref. 1, there is no contribution from the plateau parameter. This might explain why the universality in fluidity and MSD was not noted before. Referring to the simulation data in Fig. 4, one can easily imagine the plateau parameter β to be non-universal, leading to a universal inherent MSD but a non-universal full MSD. From Eq. (4) this leads to a universal real part of the fluidity, but a non-universal imaginary part. This in turn leads the more commonly studied frequency-dependent viscosity, $\eta(\omega) = 1/F(\omega)$, to become non-universal. Testing this hypothesis requires careful analysis of high quality data.

It is puzzling that particles in a liquid move like in a disordered solid. The liquid is disordered, of course, but the more or less random potential-energy landscape experienced by any given particle change with time. This argument refers to three dimensions. Taking a more abstract approach, one may argue that *complexity* may be replaced by *randomness* in the high-dimensional configuration space [34]. This way of thinking about the problem addresses also the challenge that a given particle does not experience a frozen landscape; moreover, it is difficult to justify modeling the liquid as a system of non-interacting particles in 3d. Figure 4 showed that the all-particle MSD is fitted well by the RBM prediction. Figure 5(a) shows results for the same analysis restricted to the A particles, while (b) shows it for the B particles. The fit to the RBM is not as good for the A particles as for all particles (Fig. 4), which indicates that the A particles are not accurately modeled by the RBM. Interestingly, the B particles are well fitted by the RBM. The B particles are smaller than the A particles and move faster, with a characteristic time for transition to diffusive dynamics for the B particles that is about 1/10 of that of the A particles. This means that the B particles to a higher extent than the A particles move in a frozen landscape in 3d.

In summary, we have shown that the MSD of the KA model modified to avoid crystallization follows the zero-shape-parameter RBM prediction. This confirms the experimental findings of Ref. 1 that are also well described by the RBM. Our results do not explain, however, *why* the RBM works so well, but tentatively suggest that a proper theoretical explanation should relate to the high-dimensional configuration space, not 3d space.

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