

## Hopping in a supercooled Lennard-Jones liquid: Metabasins, waiting time distribution, and diffusion

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We investigate the jump motion among potential energy minima of a Lennard-Jones model glass former by extensive computer simulation. From the time series of minima energies, it becomes clear that the energy landscape is organized in superstructures called metabasins. We show that diffusion can be pictured as a random walk among metabasins, and that the whole temperature dependence resides in the distribution of waiting times. The waiting time distribution exhibits algebraic decays:  $\tau^{-1/2}$  for very short times and  $\tau^{-\alpha}$  for longer times, where  $\alpha \approx 2$  near  $T_c$ . We demonstrate that solely the waiting times in the very stable basins account for the temperature dependence of the diffusion constant.

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The energy landscape picture that was proposed more than thirty years ago by Goldstein [1] has turned out to be a fruitful way of describing the complicated many-particle effects in disordered systems [2]. Starting from the joint potential energy landscape (PEL),  $V(x)$ , of  $N$  particles as a function of their configuration  $x = \{x_1, \dots, x_N\}$ , one expects that the properties of the system at sufficiently low temperatures will be dominated by long residences near local minima of  $V(x)$  (*inherent structures*) with rare hopping events between them [3]. Recently, it became clear for a model glass former that the strict hopping picture approximately holds for  $T < T_c$  (*landscape-dominated regime*) [4–6], where  $T_c$  is the mode-coupling temperature [7]. However, even for higher temperatures  $T < 2T_c$ , many dynamic properties are still related to the properties of inherent structures (*landscape-influenced regime*) [8–10]. Thus, in both temperature intervals, an observable like the diffusion constant  $D(T)$  should depend on the topography of inherent structures (IS) or, more generally, of basins (a basin of an inherent structure is defined as the set of configurations that reach this minimum via the steepest descent [11]). Such an understanding is indispensable to grasp the underlying physics of the Adam-Gibbs relation [12,13].

A simplified picture of glassy dynamics has been expressed in phenomenological models in Refs. [14–16] based on spatially uncorrelated hopping processes (*random walk*) in configuration space. Then the whole temperature dependence is contained in the average waiting time  $\langle \tau(T) \rangle$ . The true dynamics of glass forming systems, however, is expected to be more complicated. For example, it is known that back and forth correlations cannot be neglected and that the elementary jump distances depend on temperature [17,18]. In general, in a hopping approach, the temperature dependence of the diffusion constant may be related to spatial and temporal aspects as expressed by the relation

$$D(T) = \frac{a^2(T)}{6N\langle \tau(T) \rangle}. \quad (1)$$

With this ansatz, we anticipate the important role of the mean waiting time and collect the spatial details of hopping in an

*effective* jump width  $a(T)$ . The latter involves (i) the average jump distance, (ii) correlations of jump widths with waiting times, and (iii) directional correlations of successive jumps. To our knowledge, this decomposition into spatial and temporal contributions has not been systematically implemented within the PEL framework so far. *A priori* it is not clear to which degree the temperature dependence of  $a(T)$  is relevant; see, e.g., Refs. [19,20]. Some information about the waiting time distribution (WTD) has already been gained from the analysis of hopping processes of single particles in real space via computer simulations [21,22]. In contrast, we consider hopping in configuration space, with the advantage of incorporating the full many-particle effects [23].

In this paper, we present detailed information about the spatial and temporal aspects of hopping in a model glass former, and individually determine  $a(T)$  and  $\langle \tau(T) \rangle$ . We demonstrate that (i) *only*  $\langle \tau(T) \rangle$  depends on temperature, (ii) hopping among single basins is not a random walk, whereas hopping among superstructures of minima (metabasins) is close to a random walk, (iii)  $\langle \tau(T) \rangle$  is dominated by the long waiting times due to a slow (approximately algebraic) decay of WTDs.

In the present work, we investigate a binary mixture of Lennard-Jones particles (BMLJ), as recently treated by two groups [6,24]; see also Ref. [25]. It is characterized by the interaction potentials  $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$  with the parameter set  $N = N_A + N_B = 52 + 13 = 65$ ,  $\sigma_{AB} = 0.8\sigma_{AA}$ ,  $\sigma_{BB} = 0.88\sigma_{AA}$ ,  $\epsilon_{AB} = 1.5\epsilon_{AA}$ ,  $\epsilon_{BB} = 0.5\epsilon_{AA}$ , and  $r_c = 1.8\sigma_{AA}$ . Linear functions were added to the potentials to ensure continuous forces and energies at the cutoff  $r_c$ . Units of length, mass, energy, and time are  $\sigma_{AA}$ ,  $m$ ,  $\epsilon_{AA}$ , and  $\sqrt{m\sigma_{AA}^2/\epsilon_{AA}}$ , respectively. For convenience, though, we will omit units here. We use Langevin molecular dynamics simulations (MD) with fixed step size,  $\lambda^2 = 0.015^2 = 2k_B T \Delta t / m \zeta$ , equal particle masses  $m$ , friction constant  $\zeta$ , and periodic boundary conditions at a density of  $\rho = 1.2$ . The friction constant  $\zeta = 2/0.015^2$  is chosen so that  $\Delta t = 1/T$ . Due to the different type of dynamics, the *absolute* values of times and diffusion constants are different from those found

within Newtonian dynamics simulations. The mode-coupling temperature is  $T_c = 0.45 \pm 0.01$  in this model system (compare Ref. [25]).

For the analysis of dynamics in configuration space, it is essential to use small systems because otherwise many interesting effects will be averaged out [10]. The relevance of small systems has been also pointed out by other groups; see, e.g., Refs. [23,26]. On the other hand, the system should not be too small in order to avoid major finite-size effects.  $N \approx 60$  turns out to be a very good compromise for binary Lennard-Jones mixtures, whereas  $N \leq 40$  already displays major finite-size effects [27]. Here, we choose  $N = 65$ . To back those findings, we have carried out an extensive study of finite-size effects for systems of  $N = 65$ ,  $130$ , and  $N = 1000$  particles [28]. It turned out that the  $N = 65$  system is nearly identical to the bulk ( $N = 1000$ ) above  $T_c$ . Since well-equilibrated runs of  $N \geq 130$  are lacking below  $T_c$ , finite-size effects cannot be excluded there at the present stage. However, this does not affect the main results of this paper. More important is the question of a good equilibration at each temperature. Have the runs been long enough to sample the PEL sufficiently? Above  $T_c$  this is uncritical, which can be seen from the fact that each run comprised at least  $850 \alpha$ -relaxation times. A more detailed check, involving the lifetimes and distribution of metabasins, indicates that runs down to  $T = 0.435$  are feasible with the available computer power.

By regular quenching the MD trajectory  $x(t)$  to the bottom of the basins visited at time  $t$ , as proposed by Stillinger and Weber, we obtain a discontinuous trajectory  $\xi(t)$ . In this way, one discards the more or less complicated vibrational part  $x(t) - \xi(t)$  of motion, only keeping the visited minima as ‘‘milestones.’’ The one-particle diffusion constant can be also determined from the squared displacement of inherent structures via  $D = \lim_{t \rightarrow \infty} \langle (\xi(t) - \xi(0))^2 \rangle / 6Nt$ .

How to resolve the *elementary* hopping events? Since computer time prohibits us to calculate  $\xi(t)$  for every time step, we normally find ourselves in the situation of having equidistant quenched configurations  $\xi(t_i)$ , with, say,  $t_{i+1} - t_i \sim 10^5$  MD steps. If the same minimum is found for times  $t_i$  and  $t_j$ , we need not care about transitions in the meantime because no relaxation has occurred there. If, in contrast,  $\xi(t_i) \neq \xi(t_{i+1})$ , we must not expect  $\xi(t_{i+1})$  to be the direct successor of  $\xi(t_i)$ , since many other minima could have been visited between  $t_i$  and  $t_{i+1}$ . Therefore, further minimizations in this time interval are necessary. For reasons of efficiency, we apply a straightforward interval bisection method, which locates all relevant transitions with an accuracy of 1 MD step. Although computationally demanding, this has proven to be most efficient for resolving the relevant details of hopping on the PEL.

As demonstrated in Ref. [10], the time series of potential energies  $\epsilon(t) = V(\xi(t))$  reflects well the character of dynamics in the supercooled state. For  $T = 0.435$ ,  $\epsilon(t)$  is shown in Fig. 1, from which we note a remarkable structure in  $\epsilon(t)$ . The system is trapped in some stable configurations for long times, during which a small number of minima are visited over and over again. Obviously, these minima form superstructures, which, following Ref. [3], we denote *metabasins*

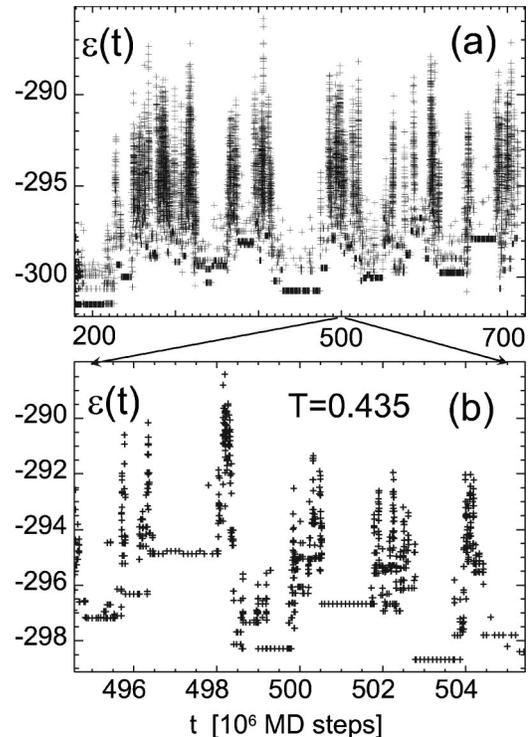


FIG. 1. The time series of minima energies measured for the BMLJ system of  $N = 65$  particles,  $T = 0.435$ . The distance between minimizations before interval bisection is  $10^5$  MD steps. The length of the total run is  $2 \times 10^9$  MD steps. (a) Time window covering a quarter of the total run (b) magnification by a factor of 50.

(MBs). One may imagine that minima of the long-lived MBs are organized in funnel-like structures so that the system is stuck there for a long time. It has been argued that the occurrence of  $\beta$  relaxation at low temperatures is due to such substructure of the PEL [3]. This is supported by the real-space signature of MBs as reported by Middleton and Wales [29]. Formally, there is no unique way to define MBs for a given PEL due to the lack of a strict time scale separation. Here, we take the pragmatic view and let the system decide by its MD run. The intuitive notion of MBs from Fig. 1 can be cast into an algorithm in a straightforward way, see Refs. [10,36]. One major advantage of analyzing MBs rather than basins is that the charming simplistic picture of a random walk in configuration space will be better fulfilled since direct back and forth correlations are already taken into account. It turns out (see Fig. 1) that long-lived stable MBs are separated by bursts of rapid transitions among higher minima which look like fountains. They cannot be detected without interval bisection. The waiting times of the MBs range from a few MD steps to many millions of them. Moreover, comparing Figs. 1(a) and 1(b), we find a certain self-similarity in  $\epsilon(t)$  when inspected on different time scales. The distribution of MB lifetimes  $\tau$  will be denoted  $\varphi(\tau, T)$ , its first moment  $\langle \tau(T) \rangle$  being a key quantity for the following considerations.

Our goal is to find an expression for the effective jump width  $a(T)$  of Eq. (1). To this end, as a generalization of  $\xi(t)$ , we define the MB inherent structure  $\xi_{\text{MB}}(t)$  as the

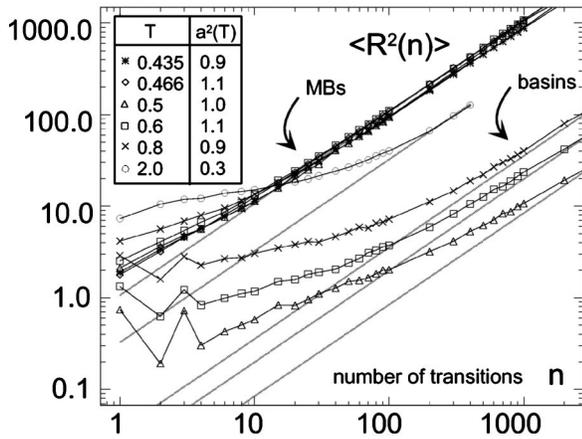


FIG. 2. Squared displacement  $\langle R^2(n) \rangle$  after  $n$  MB jumps for the temperatures  $T=0.435, 0.466, 0.5, 0.6, 0.8,$  and  $2.0$ . Also shown are three curves ( $T=0.5, 0.6,$  and  $0.8$ ) for jumps among single basins (lower curves). The latter data have been obtained by extremely frequent minimizations, which resolve nearly all IS transitions. We have included lines of slope 1.

mean of  $\xi(t)$  over the MB lifetime. The key idea now is to introduce the squared distance  $\langle R^2(n) \rangle$  after  $n$  jumps [30], averaged over different realizations. This quantity is purely spatial since it does not involve any time scale. In the limit of large  $n$ , one obtains due to the central limit theorem  $\lim_{n \rightarrow \infty} \langle R^2(n) \rangle / \langle \xi_{\text{MB}}^2(n \langle \tau \rangle) \rangle = 1$ , where  $\langle \xi_{\text{MB}}^2(n \langle \tau \rangle) \rangle$  is the average squared displacement after time  $n \langle \tau \rangle$ . Thus,

$$D(T) = \lim_{n \rightarrow \infty} \frac{\langle \xi_{\text{MB}}^2(n \langle \tau \rangle) \rangle}{6Nn \langle \tau \rangle} = \left[ \lim_{n \rightarrow \infty} \frac{\langle R^2(n) \rangle}{6n} \right] \frac{1}{N \langle \tau \rangle},$$

where the first factor may be identified as  $a^2(T)/6$ . Note that both factors are independent of system size because IS transitions are localized [ $\langle R^2(1) \rangle = O(1)$ ] and mean waiting times decrease with system size [ $\langle \tau \rangle = O(1/N)$ ]. We may now calculate  $a(T)$  from the simulations, results are shown in Fig. 2. The most important observation is that  $a(T)$  is temperature independent for  $T < 1$ . Interestingly, this is not affected by the variation of the elementary jump width  $\langle R^2(1) \rangle$ , which increases with temperature, a fact that was recently observed by Schulz *et al.* [18]. A possible explanation for this might be found in the increasing population of higher-order stationary points [5], which are known to be more distant to neighboring minima, but also provoke many “bookkeeping” IS transitions, thus resulting in larger backward correlations [23].

In any event, the constancy of  $a(T)$  in the landscape-influenced regime  $T < 1$  implies that the temperature dependence of  $D(T)$  follows alone from  $\langle \tau(T) \rangle$ , i.e.,  $D(T) \propto 1/\langle \tau(T) \rangle$ . This simple picture breaks down for  $T > 1$ , where the explored regions of configuration space probably have a completely different structure. It has to be noted that the constancy of  $a(T)$  for low  $T$  relies heavily on our resolution of *all* elementary IS transitions leading to relaxation.

A further insight from Fig. 2 is that the dynamics on the level of MBs is basically a random walk except for minor

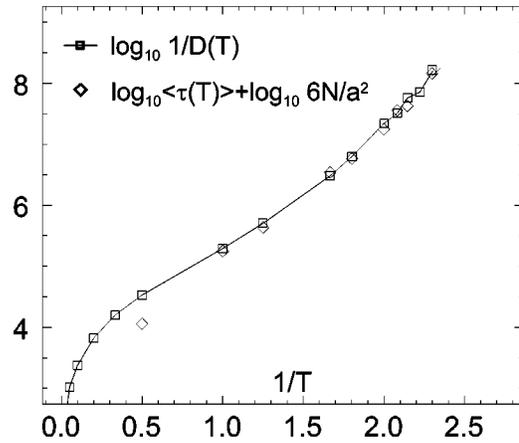


FIG. 3. Arrhenius plot of the inverse one-particle diffusion constant  $1/D(T)$  and the mean waiting time  $\langle \tau(T) \rangle$  multiplied by a constant ( $a^2=1.0$ ). Error bars are of the order of the symbol size.

back correlations for  $n \leq 5$ . As seen from the figure, these correlations are present between *single* basins, the consequence being a significant deviation from the relation  $\langle R^2(n) \rangle \propto n$ . Also note the oscillations in the single basin  $\langle R^2(n) \rangle$  at small  $n$ , which result from the back-and-forth motion within MBs. More importantly, the single basin curves do not have the same large- $n$  limit so that the effective jump length on the level of single-basins would be temperature dependent. It remains unclear why for a very small LJ system ( $N=32$ ), correlations among adjacent basins are irrelevant for  $T \approx T_c$  [23], and why intra-basin rather than interbasin dynamics is deemed to be the key to the understanding of diffusion [31].

We can check the relation  $D \propto 1/\langle \tau \rangle$  within our simulations. Figure 3 shows that it is indeed well fulfilled for  $T < 1$  while for  $T=2$ , we find the expected deviations.

In the remaining part of the paper, we discuss the properties of the WTDs  $\varphi(\tau, T)$ , see Fig. 4. For short  $\tau$ , all curves

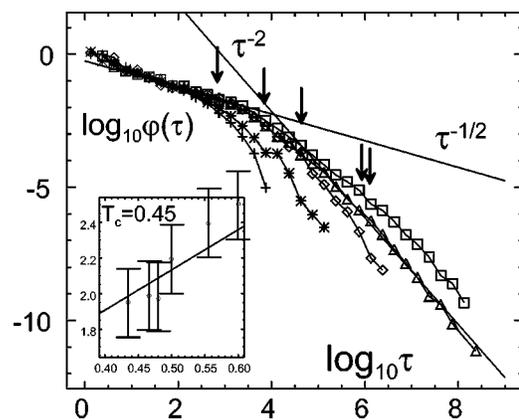


FIG. 4. Distributions of waiting times,  $\varphi(\tau, T)$ , for  $T=1.0, 0.8, 0.6, 0.5,$  and  $0.435$  (from left to right). Curves have been shifted to overlap for small  $\tau$ . Lines corresponding to algebraic decays with exponents 0.5 and 2 are shown as guides to the eye. The arrows mark  $\tau^*(T)$ , i.e., the waiting time with the property  $\int_{\tau^*(T)}^{\infty} d\tau \varphi(\tau) \tau = 0.9 \langle \tau \rangle$ . Inset: Power-law exponent  $\alpha(T)$  from fits to the long-time decay. Within the possible accuracy,  $\alpha(T) \approx T/T_c + 1$ .

exhibit a power-law behavior with exponent  $-1/2$ , similar to Ref. [32]. At  $\tau \approx 10^3 - 10^4$ , a crossover to the faster decay  $\varphi(\tau, T) \propto \tau^{-\alpha(T)}$  can be observed. For  $T \approx 0.45$ , one finds  $\alpha \approx 2.0$ , for which the expectation value  $\langle \tau \rangle$  would diverge. However, the behavior  $\varphi(\tau) \propto \tau^{-\alpha}$  cannot extend to infinity. Due to the finite number of MBs in the system, there exists a maximum effective barrier  $E_{\max}$  giving rise to an exponential cutoff at some minimum rate  $\gamma_{\min}$ .

The slow decay of the WTDs leads to the important observation that the mean waiting time  $\langle \tau \rangle$  is dominated by the contributions from large  $\tau$  (see arrows in Fig. 4). For example, at  $T = 0.435$ , 90% of  $\langle \tau \rangle$  are formed by the 6% longest waiting times, which are basins of lifetimes greater than  $0.5 \times 10^6$  MD steps. This may come as a surprise because (i) the short-lived MBs are much more numerous than the long-lived and (ii) one might intuitively think that the diffusion constant and, thus,  $\langle \tau \rangle$  is dominated by the fast particles. The result is in qualitative agreement with the approach of Xia and Wolynes who regard the relaxation of long-lived local structures as the time-determining step [33].

Interestingly, the algebraic decay of the WTDs follows for some theoretical models of diffusion with builtin traps. This is the case for Bouchaud's trap model [16] and the trapping diffusion model of Odagaki *et al.* [15]. A recent comparison of WTDs in the Lennard-Jones system with that of trap models can be found in Ref. [34].

In conclusion, the detailed analysis of hopping on the PEL has provided different insights into the mechanism of diffusion in supercooled liquids. As we have seen, the emergence of long-lived MBs is the reason for the slowing down of molecular motion in our supercooled model liquid. As a next step, the waiting time should be related to the respective MB energies to establish a connection between energy (thermodynamics) and dynamics in the spirit of the Adam-Gibbs relation (see the subsequent paper [35]).

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 [36] It is important to note that, different from Ref. [10], we will treat all MBs on the same footing here, no matter if they contain one or many minima.