From elementary steps to structural relaxation: A continuous-time random-walk analysis of a supercooled liquid

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(Received 24 February 2008; published 21 July 2008)

We show that the dynamics of supercooled liquids, analyzed from computer simulations of the binary mixture Lennard-Jones system, can be described in terms of a continuous-time random walk (CTRW). The required discretization comes from mapping the dynamics on transitions between metabasins. This yields a quantitative link between the elementary step and the full structural relaxation. The analysis involves a verification of the CTRW conditions as well as a quantitative test of the predictions. The wave-vector dependence of the relaxation time and the degree of nonexponentiality can be expressed in terms of the first moments of the waiting time distribution.

DOI: 10.1103/PhysRevE.78.011504 PACS number(s): 64.70.Q−

The dynamics of supercooled liquids is a very complex process with many nontrivial features such as nonexponential relaxation, decoupling of diffusion and relaxation, significantly correlated forward-backward processes (e.g., the cage effect), and increasing length scales of relaxation, just to mention some of the most prominent [1–3]. The complexity of the dynamics originates from the highly cooperative nature of the dynamical processes.

Several phenomenological models have been proposed that attempt to describe the dynamics of supercooled liquids in relatively simple terms, thereby implying some kind of coarse-graining to get rid of the microscopic details of the dynamics. In the free-energy [4–7] and the random first order transition (RFOT) models [8] the system relaxes, possibly in a multistep process, between different states. One prominent example is the trap model [5,6], postulating a sequence of escape processes where the waiting time τ in a configuration is fully governed by its energy and the new configuration is randomly chosen from the set of all possible configurations. Thus, the dynamics is fully described by the waiting time distribution $\varphi(\tau)$. Extending this model by the spatial aspects of the relaxation processes one would, in its simplest version, end up with a continuous-time random walk (CTRW). Note that, in general, continuous-time random walks [6,9–11] as well as the related Levy walks [12,13] are often used to describe anomalous dynamic properties, characterized by nontrivial power-law behavior of quantities such as the mean-square displacement.

In recent years the facilitated spin models have been revitalized to grasp the dynamics of supercooled liquids [14–17]. They are thought to reflect the heterogeneous mobility field of molecular glass-forming systems. One spin corresponds to a small volume which is either unjammed or jammed (spin up or down). The ability of a spin to flip is exclusively governed by the orientation of the adjacent spins. Self-diffusion has been introduced by postulating a random walk of the particle with the chance to move if the old as well as the new site is mobile [17–19]. This dynamics is also described in terms of a CTRW, although for the model variant (East model) supposed to describe fragile systems a direct mapping is not possible [18].

Use of the CTRW picture in the context of these phenomenological models does not necessarily imply that it is of relevance for microscopic glass-forming systems. Here we analyze a binary mixture Lennard-Jones system (BMLJ), a standard model of supercooled liquids [20], via computer simulations. The goal of this work is threefold. First, we explicitly show that the required conditions for the applicability of the CTRW approach are satisfied to a very good approximation. Second, we prove that the CTRW approach allows one to obtain not only the wave-vector-dependent relaxation time (as already discussed, e.g., in [18]) but also the nonexponentiality of relaxation. Third, the predictions are verified by explicit comparison with the numerical simulations.

We analyze a BMLJ system with $N=65$ particles at $T=0.5$, which is slightly above the mode-coupling temperature. It has been shown that this system is large enough to recover the diffusion constant without significant finite-size effects in the range of temperatures accessible by computer simulations [21,22]. Details of the model are described elsewhere [20,21]. The discretization of the dynamics, required for the application of the CTRW approach, results from the use of inherent structures, i.e., local minima of the potential energy landscape [23,24], or the use of metabasins (MBs) [22,25]. Of particular relevance in this work is the incoherent scattering function $S(q,t)=\langle \cos q[x(t+t_0)-x(t_0)]\rangle$ where the angular brackets denote the average over all particles and all t_0. Furthermore, $x(t)$ is the x coordinate of a particle. The first decay at short times to a value $f<1$ is due to the fast β relaxation, whereas the long-time relaxation reflects the α relaxation. It is often described by a Kohlrausch-Williams-Watts (KWW) function $f\exp[-(t/\tau_{\mathrm{KWW}})^{\beta_{\mathrm{KWW}}}]$. When analyzing $S(q,t)$ for the sequence of inherent structures rather than actual configurations it turns out at temperatures close to the mode-coupling temperature that the short-time decay disappears and the decay is fully related to the α relaxation with identical values τ_{KWW}, β_{KWW} [26]. Not surprisingly, the same holds for the sequence of MBs (data not shown). From now on, $S(q,t)$ will represent the case of MBs, thereby describing the α relaxation.

Two important observables enter the CTRW approach: (i) the waiting time distribution $\varphi(\tau)$ and (ii) the probability $\pi_1(x)$ that a particle during a transition between two MBs

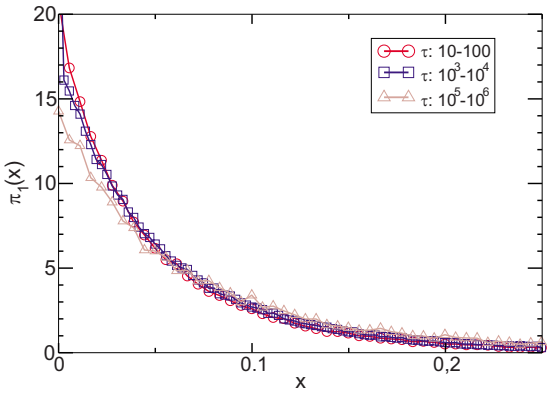

FIG. 1. (Color online) $\pi_1(x)$ for different values of the waiting times before the corresponding MB transition. Within statistical uncertainty $\pi_1(x)$ does not depend on the waiting time.

moves a specific distance along some fixed direction (here x). More generally, $\pi_n(x)$ expresses the corresponding probability after n MB transitions. The Fourier transform is denoted $\pi_n(q)$. Under conditions (C1)–(C3), which form the basis of the CTRW approach and are discussed below, it is possible to express $S(q,t)$ in terms of $\varphi(\tau)$ and $\pi_1(q)$.

(C1) $\pi_1(x)$ *does not depend on the waiting time since the previous transition*. From the data in Fig. 1 the validity of (C1) directly emerges. Only for the longest waiting times, which have only a very low probability (as reflected by the noise), minor deviations occur. As a consequence the spatial and temporal contributions separate to a very good approximation and one can write

$$S(q,t) = \lim_{N\to\infty} S_N(q,t) = \lim_{N\to\infty} \sum_{n=0}^{N} S_n(t)\pi_n(q). \tag{1}$$

Here $S_n(t)$ denotes the probability to have exactly n transitions during time t. This is the central equation of the CTRW because it expresses the total dynamics during time t in terms of discrete processes with well-defined probabilities.

(C2) *Successive waiting times are statistically uncorrelated so that the time evolution can be regarded as a sequence of randomly chosen waiting times.* This has already been shown in Ref. [27]. Therefore $S_n(t)$ can be expressed in terms of the waiting time distribution $\varphi(\tau)$ [18,28] [see Eq. (8) below]. Using the numerically determined $\varphi(\tau)$ and $\pi_n(q)$, one can compare $S(q_{\max},t)$, obtained from simulation, with the estimation Eq. (1) where $q_{\max}$ is the maximum of the structure factor; see Fig. 2. The agreement is very good except for minor deviations for very long times. Of the order of 10^2 MB transition processes are required to have complete relaxation. Due to the resulting average effect a possible violation of (C1) would not hamper the CTRW analysis.

(C3) *Subsequent transitions are spatially uncorrelated.* The underlying Markov hypothesis can be formally written as

$$\pi_n(x) = \int dx'\, \pi_{n-1}(x')\pi_1(x-x'). \tag{2}$$

In Fourier space this convolution reads

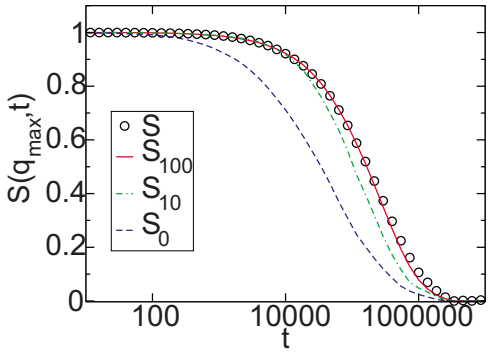

FIG. 2. (Color online) Comparison of the actual incoherent scattering function $S(q_{\max},t)$ with the estimated function $S_N(q_{\max},t)$ for different values of N.

$$\pi_n(q) = \pi_1(q)^n. \tag{3}$$

Strict validity of (C3) implies among other things a linear dependence of the mean square displacement (MSD) on the number of MB transitions. However, in [21] a slightly nonlinear behavior has been observed [$a^2 \equiv \lim_{n\to\infty}(1/n)\langle x^2\rangle_{\pi_n} = 0.005$ differs from $\langle x^2\rangle_{\pi_1} = 0.009$ [21], using the notation $\langle x^2\rangle_f \equiv \int dx\, x^2 f(x)$]. This deviation reflects the presence of minor forward-backward correlations. However, due to the local nature of forward-backward transitions, one may expect that for length scales significantly beyond a the correlated forward-backward jumps become irrelevant. To check this in detail, we have analyzed the n dependence of $\pi_n(q)$, shown in Fig. 3 for different values of the wave vector q. Interestingly, for $q=q_{\max}$ the limiting behavior $\pi(q) \equiv [\pi_n(q)]^{1/n} = \text{const}$ is already reached for $n \geq 5$, as reflected by the straight line. For smaller q values, Eq. (3) holds even better. Since in the range of relevant q values one has $a^2q^2 \ll 1$, the term $\pi(q)$ can be approximated by $1-q^2a^2/2$, using a simple Taylor-expansion argument. Actually, using inherent structures rather than MBs, the large-n regime would be reached only for $n \approx 10^3$ [21]. This would strongly invalidate (C3).

Using (C1)–(C3), and substituting all $\pi_n(q)$ by $\pi(q)$, the temporal Laplace transform of the incoherent scattering function, i.e., $S(q,\lambda)$, can be calculated analytically, yielding the Montroll-Weiss equation [9]. Unfortunately, the inverse

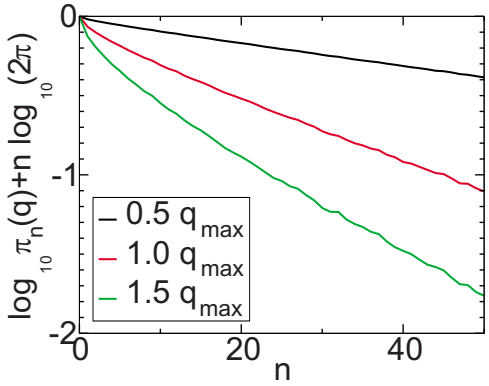

FIG. 3. (Color online) n dependence of $\pi_n(q)$ for different values of q.

Laplace transform of $S(q,\lambda)$ cannot be analytically performed to calculate $S(q,t)$. Therefore we proceed in a somewhat different way. First, we define

$$\tau_0(q) \equiv \int dt\, S(q,t) \tag{4}$$

and

$$\beta_m(q) \equiv \frac{\tau_0^2(q)}{\int dt\, tS(q,t)}. \tag{5}$$

$\tau_0(q)$ denotes the relaxation time at wave vector q and β_m reflects the shape of $S(q,t)$, based on the different moments. Whereas for exponential relaxation one has $\beta_m=1$, it decreases when $S(q,t)$ decays in a nonexponential manner. In case of KWW relaxation one has $\beta_m=\Gamma^2(1/\beta_{\mathrm{KWW}})/[\beta_{\mathrm{KWW}}\Gamma(2/\beta_{\mathrm{KWW}})]$ where $\Gamma(\,)$ denotes the Γ function (e.g., $\beta_{\mathrm{KWW}}=1/2$ corresponds to $\beta_m=1/3$). β_m depends monotonically on β_{KWW}. Thus, β_m is a measure of the degree of nonexponentiality.

Our goal is to find simple expressions for $\tau_0(q)$ and $\beta_m(q)$. For this purpose one can introduce the *persistence time* distribution $\xi(\tau)$. It denotes the probability that for a random starting point in time the next transition occurs a time τ later [9,19]. It is related to the waiting time distribution via

$$\xi(\tau) = \int_\tau^\infty dt'\, \varphi(t')/\langle\tau\rangle_\varphi. \tag{6}$$

Furthermore, it is related to $S_0(t)$ via

$$S_0(t) = \int_t^\infty dt'\, \xi(t'). \tag{7}$$

For $n>0$ the Laplace transform of $S_n(t)$ is given by

$$S_n(\lambda) = \xi(\lambda)^2\varphi(\lambda)^{n-1}/\langle\tau\rangle_\varphi. \tag{8}$$

Straightforward calculation yields $\int dt\, S_n(t)=S_n(\lambda=0)=\langle\tau\rangle_\varphi$ for $n>0$. Note that for two functions, connected by $f(t)=\int_t^\infty dt'\, g(t')$, one obtains

$$\langle t^n\rangle_f = \frac{\langle t^{n+1}\rangle_g}{n+1}. \tag{9}$$

This implies $\int dt\, S_0(t)=\langle\tau\rangle_\xi$, i.e., the average persistence time. Using again Eq. (9) it can be also expressed as $\langle\tau^2\rangle_\varphi/\langle\tau\rangle_\varphi$. Note that $\langle\tau\rangle_\xi/\langle\tau\rangle_\varphi \gg 1$ for a broad waiting time distribution, reflecting large dynamic heterogeneities. Equivalently, this means that the time until the first transition after a randomly chosen time takes much longer than the typical time $\langle\tau\rangle_\varphi$ between successive jumps.

Using Eq. (1) together with Eqs. (3) and (9), one obtains [18]

$$\tau_0(q)/\langle\tau\rangle_\varphi = \frac{\langle\tau\rangle_\xi}{\langle\tau\rangle_\varphi} + \frac{\pi_1(q)}{1-\pi_1(q)} \approx \frac{\langle\tau\rangle_\xi}{\langle\tau\rangle_\varphi} + \frac{2}{q^2a^2}. \tag{10}$$

We note in passing that $\langle\tau\rangle_\xi$ can be identified with the structural relaxation time τ_α [18]. To determine the simulated $\tau_0(q)$ via integration over $S(q,t)$ we first fitted $S(q,t)$ by a sum of two stretched exponentials and then performed the integration analytically.

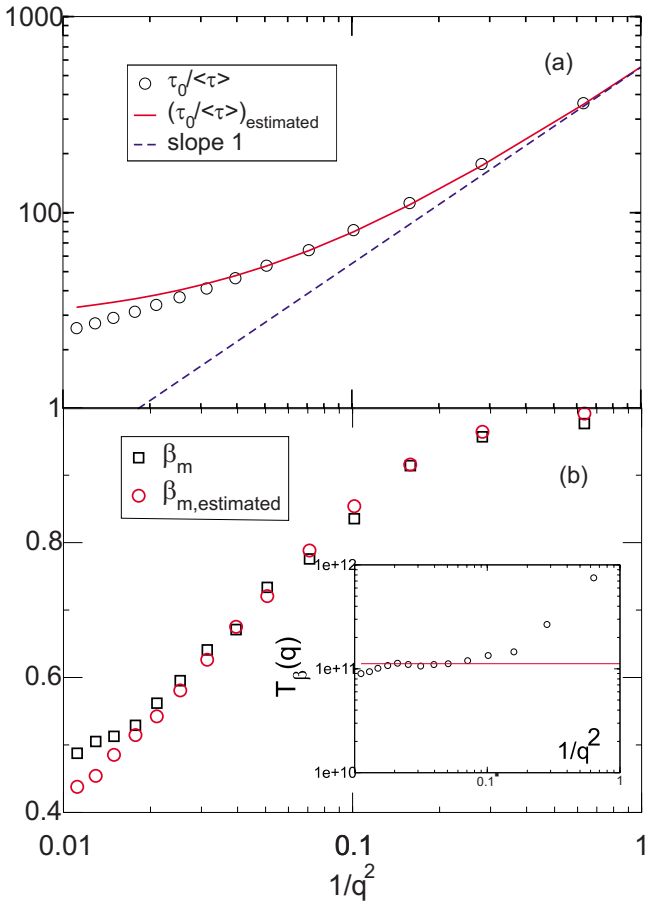

FIG. 4. (Color online) q dependence of (a) $\tau_0(q)$ together with its estimation via Eq. (10) and (b) of $\beta_m(q)$ together with its estimation. In the inset the validity of the theoretical expectation $(d/dq)T_\beta(q)=0$ is tested.

In Fig. 4(a) we show the comparison with the simulated data. We used $\langle\tau\rangle_\xi/\langle\tau\rangle_\varphi=27$, as determined from the numerically determined waiting time distribution. The q dependence of $\tau_0(q)$ is qualitatively similar to the data reported in [29] and [30]. Note, however, that with the present definition of $\tau_0(q)$ and the reference to the MB dynamics for the definition of $\varphi(\tau)$ and a^2, a parameter-free prediction of the q dependence becomes possible. At large q ($q>q_{\mathrm{max}}$), the system relaxes somewhat faster because the effective value of a^2 increases due to the relevance of forward-backward correlations (see above). For smaller q, given by $1/q^2 \approx \langle\tau\rangle_\xi/\langle\tau\rangle_\varphi a^2/2$, there is a crossover of $\tau_0(q)$ from the q-independent large-q limit to the small-q limit $\tau_0(q)=2\langle\tau\rangle_\varphi/(q^2a^2)$. Thus, for large dynamic heterogeneities, i.e., low temperatures, this crossover may happen at quite large distances [18]. Similarly, these nontrivial features are also reflected by a specific time evolution of the self-part of the van Hove function $G_s(x,t)$ [31]. The deviations of $G_s(x,t)$ from simple diffusion have been analyzed in detail in [32].

For the discussion of $\beta_m(q)$ we first rewrite Eq. (5) as

$$\beta_m^{-1}(q) - 1 = T_\beta(q)/\tau_0^2(q) \tag{11}$$

with $T_\beta(q) = \int dt\, tS(q,t) - \tau_0^2(q)$. Following the standard derivation of the Montroll-Weiss equation, one can show, after a tedious but straightforward calculation with the ingredients presented in this work, that $(d/dq)T_\beta(q)=0$ [28], i.e., $T_\beta(q) \equiv T_\beta$. For the evaluation of T_β we choose the limit $q \to \infty$ where $S(q,t)=S_0(t)$. Following Eq. (9) the first term equals $\langle \tau^2 \rangle_\xi / 2$ whereas the second term is given by $\langle \tau \rangle_\xi^2$, i.e.,

$$T_\beta(q) = \frac{\langle \tau^2 \rangle_\xi}{2} - \langle \tau \rangle_\xi^2, \tag{12}$$

which directly reflects the width of the persistence time distribution. Note that via Eq. (9) T_β involves the third moment of the waiting time distribution $\varphi(\tau)$. Interestingly, the q dependence of $\beta_m(q)$ is fully governed by $\tau_0(q)$. Thus, the degree of nonexponentiality displays exactly the same crossover behavior as the relaxation time. A comparison of Eqs. (11) and (12) with the numerical data is shown in Fig. 4(b), showing again a good agreement. Actually, due to the extreme dependence of the third moment on the fine details of the long-time behavior of $\varphi(\tau)$, a precise estimation of T_β from $\varphi(\tau)$ is not possible. Again, the deviations at large q reflect the more complicated dynamics at short length scales. The deviations for small q come from the trivial fact that $T_\beta(q)$ results from a difference of two very large numbers which, because of the nearly exponential behavior, are very similar.

In summary, the present work has shown that the CTRW approach, more or less explicitly used in different models of the glass transition, can indeed be *numerically derived* for an atomic glass-forming system. This shows that after an appropriate coarse-graining procedure (here, the metabasins) the complex dynamics of supercooled liquids is fully determined by the properties of the elementary steps. On a lower level of coarse graining, namely, the inherent structures, (C3) and thus the CTRW approach are strongly violated.

We gratefully acknowledge the support by the DFG via SFB 458 and helpful discussions with L. Berthier.

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