Dynamic Entropy as a Measure of Caging and Persistent Particle Motion in Supercooled Liquids

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(Phys. Rev. E: submitted 12/18/98; revised 07/20/99)

The length-scale dependence of the dynamic entropy is studied in a molecular dynamics simulation of a binary Lennard-Jones liquid above the mode-coupling critical temperature $T_c$. A number of methods exist for estimating the entropy of dynamical systems and we utilize an approximation based on calculating the mean first-passage time (MFPT) for particle displacement because of its tractability and its accessibility in real and simulation measurements. The MFPT dynamic entropy $S(h)$ is defined to equal the inverse of the average first-passage time for a particle to exit a sphere of radius $h$. This measure of the degree of chaotic motion allows us to identify characteristic time and space scales and to quantify the increasingly correlated particle motion and intermittency occurring in supercooled liquids. In particular, we identify a “cage” size defining the scale at which the particles are transiently localized, and we observe persistent particle motion at intermediate length scales beyond the scale where caging occurs. Furthermore, we find that the dynamic entropy at the scale of one interparticle spacing extrapolates to zero as the mode-coupling temperature $T_c$ is approached.

I. INTRODUCTION

It has been suggested that the glass transition in cooled liquids is a dynamic transition from an ergodic to a non-ergodic state. For example, the ideal mode-coupling theory predicts that the molecules of simple liquids become increasingly “caged” by surrounding molecules, resulting in an ergodic to non-ergodic transition at a critical temperature $T_c$ at which the fluid molecules become permanently localized (i.e., the self-diffusion coefficient vanishes) [1]. Although a tendency toward particle localization for increasingly long times has been observed in simulations and experiments on supercooled liquids, particle localization and structural arrest does not actually occur at the extrapolated temperature $T_c$ because the particles are eventually able to “escape” their cages. Recent simulations have also shown the tendency for particle motion to occur in an increasingly correlated way in supercooled liquids [2–8], a feature emphasized by the older, phenomenological Adam-Gibbs model of glass formation [9]. The observed greater particle mobility near $T_c$ is presumably a consequence of the increased collective motion of cooled liquids (“hopping” in the extended version of the mode-coupling theory [1]) which restores the ergodicity of the liquid for some temperature range below $T_c$. This thermally activated collective motion apparently postpones the ergodic to nonergodic transition to a lower temperature. In the Adam-Gibbs model [9], this lower temperature corresponds to the conjectured “ideal” glass transition temperature $T_0$, where the equilibrium configurational entropy extrapolates to zero [1].

If glass formation indeed represents an ergodic to non-ergodic dynamic transition, then it is important to derive a dynamical measure of order that quantifies both the “closeness” of the transition [1], and the degree of correlated motion in an equilibrium glass-forming liquid. Ergodic theory provides us with a natural measure in the form of the “dynamic entropy” [2–7].

The concept of dynamic entropy was introduced by Shannon in his theory describing the capacity of ideal communication devices to transmit information [10]. This idea was later developed by Kolmogorov and others [11] into a general measure of the “degree of randomness” or “degree of chaos” of dynamical systems. According to Pessin’s theorem [10], the Kolmogorov-Sinai dynamic entropy $h_{KS}$ for a Hamiltonian dynamical system equals the sum of the positive Lyapunov exponents [12,13]. These exponents are measures of the “instability” of the system evolution [12,14]. Dynamic entropy extends the equilibrium definition of entropy from statistical mechanics to the time domain. The dynamical entropy provides an estimate of the rate of growth of “information” (per unit time) required to describe the evolution of a dynamical system [11,12] and it is also a measure of the “complexity” of a dynamical system [22]. The dynamic entropy characteristically decreases as a system orders and its exploration of its phase space becomes more restricted [23,24]. Thus, the dynamic entropy decreases as a fluid crystallizes or a spin system orders [25,27].

The Kolmogorov-Sinai dynamic entropy has some shortcomings in the description of complex configurational changes that occur in supercooled liquids. In particular, $h_{KS}$ diverges for the ideal process of Brownian motion (due to the non-differentiability of the trajectories) [11,22,23]. Consequently, we must anticipate diffic-
difficulties in applying dynamic entropy to quantify particle motions at large length and time scales in the case of supercooled liquids. Recently, there has been an important generalization of the dynamic entropy concept that provides a “bridge” between microscopic dynamical system descriptions and macroscopic stochastic descriptions of liquid dynamics. This generalization recognizes that the amount of information required to describe the paths of liquid dynamics. This generalization of the dynamic entropy concept that provides a “bridge” between microscopic dynamical systems such as liquids depends strongly on the length scale of observation $\epsilon$. The $\epsilon$-dependent dynamic entropy $h(\epsilon)$ of Gaspard and Wang and others [14] (also called “$\epsilon$-entropy”) reduces to the $h_{KS}$ entropy in the limit of small $\epsilon$,

$$\lim_{\epsilon\to 0} h(\epsilon) = h_{KS}, \quad (1.1)$$

and is well-defined for idealized stochastic processes at a fixed, nonvanishing $\epsilon$. The dynamic entropy of a Brownian particle $h_B(\epsilon)$ obeys the scaling relation

$$h_B(\epsilon) \propto \epsilon^{-2}, \quad \epsilon > 0, \quad (1.2)$$

where the proportionality constant is fixed by the particle diffusion coefficient [14]. As mentioned above, $h(\epsilon)$ for stochastic particle motion diverges as $\epsilon \to 0$ and the exponent reflects the fractal dimension of the particle trajectories $[14,30]$. Specifically, the exponent 2 in Eq. (1.2) is the Hausdorff dimension of a Brownian path in three dimensions $[31]$, and in the limit of perfectly coherent (ballistic) particle motion this exponent is 1. In idealized stochastic processes (e.g. fractional Brownian motion, Lévy flights, etc.) the exponent in Eq. 1.2 can be identified with the path Hausdorff dimension $[13,14,30,32]$, and can take values intermediate between 1 and 2. This exponent reflects the “degree of persistence” in the particle displacement relative to Brownian motion.

The scale dependent dynamic entropy $h(\epsilon)$ for complex dynamical systems such as liquids depends strongly on the observational scale $\epsilon$. At very small $\epsilon$ the microscopic chaotic motion of the molecules is observed, so that $h(\epsilon)$ varies slowly with $\epsilon$. The decorrelation of particle velocities in a liquid occurs at a time and space scale corresponding to the average interparticle “collision time” and $h(\epsilon)$ starts varying with $\epsilon$ as this decorrelation occurs. This helps us to identify a characteristic space and time scale over which the bare microscopic dynamics can be coarse-grained by a stochastic description. Correlations associated with particle displacement arise at longer times in cooled liquids and $h(\epsilon)$ also helps us in determining the spatial and time scales over which these correlations occur. $h(\epsilon)$ thus provides a measure of the degree of chaotic motion appropriate to the description of real systems at arbitrary observational scales and is an attractive tool for quantifying the increasingly restricted motion in cooled liquids. It is notable that its definition is not restricted to circumstances where statistical mechanical equilibrium exists, so that this measure of the degree of chaos extends to non-equilibrium situations such as the glass state and turbulent fluids [14].

The calculation of $h(\epsilon)$ [14] (or $h_{KS}$) is generally difficult, especially in cases where $h_{KS}$ is small and long computational times are required for its accurate determination [14,25]. In the present paper, we utilize a simple approximation for $h(\epsilon)$ that has the advantage of being accessible in experiments on real materials and computer simulations [14,32]. Provided that the spatial scale $\epsilon$ is not too small [14], $h(\epsilon)$ can be approximated by enclosing the particle position at time $t = 0$ by a sphere of radius $\epsilon$ centered on the particle, and then determining the time $\tau$ at which the trajectory first arrives at the threshold distance $\epsilon$ (see Fig. 1). We average this “first-passage time” over all particles in the liquid to obtain the mean first-passage time (MFPT) $\tau(\epsilon)$ and we define the “MFPT dynamic entropy” $S(\epsilon)$ as,

$$S(\epsilon) \equiv 1/\tau(\epsilon), \quad (1.3)$$

where

$$\tau(\epsilon) = \int_0^\infty dt P_\epsilon(t), \quad (1.4)$$

$P_\epsilon(t)dt$ is the probability that the particle reaches the distance $\epsilon$ between $t$ and $t + dt$. The dynamic entropy $S(\epsilon)$ is thus one measure of the average “escape rate” of a particle from its local environment [34]. We note that although the definition of $S(\epsilon)$ is motivated by dynamical systems theory concepts, this property defines an independently interesting measure of correlated motion in liquids that does not rely on the approximation relating $S(\epsilon)$ to $h(\epsilon)$.

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to the present work. There it was established that transient clusters of highly “mobile” particles form in the cooled liquid and that the average size of these clusters grows rapidly as $T_c$ is approached. A pair distribution function for particle displacements was defined and this quantity exhibits a growing length scale upon cooling that reflects the clustering of mobile particles. The growing length scale is time-dependent and attains a peak value at a time in the $\alpha$-relaxation regime.

It has also been shown in the present liquid that the particle strings within the mobile particle clusters move in cooperatively rearranging “strings”. Notably, the string-like collective motion also begins well above $T_c$, but the strings themselves exhibit no tendency to grow rapidly near $T_c$. Instead, the length distribution of the strings is found to be nearly exponential and a similarity of this distribution to that commonly observed in equilibrium polymerization has been noted. Donati et al. have suggested that the growing barrier height to particle motion is proportional to the average string length, which would imply that these string-like motions have a basic significance for understanding transport in cooled liquids. Thus, string-like correlated particle motion appears to be an important mode of motion in our cooled liquid and part of the motivation of the present work is to better characterize the development of this type of collective motion. We are also interested in the extent to which particle displacement becomes intermittent in time in cooled liquids, since a growing intermittency in particle motion has been suggested to underlie the glass transition.

The paper is outlined as follows. In Section II we review some details of the MD simulation data utilized in this work. Section III examines $S(\epsilon)$ over a broad range of scales, and dynamical regimes are defined where the motion is ballistic, transiently localized, persistent and diffusive. These regimes are examined in separate subsections. We summarize our findings in Section IV.

II. SIMULATION DETAILS

The system studied is a three-dimensional binary mixture of 8000 Lennard-Jones (LJ) particles in which the sizes of the particles and the interaction parameters are chosen to prevent crystallization and demixing. The size of the A-particles is about 10% larger than that of the B-particles (while the mass is the same) and the particles have a relative concentration 80:20 of A-particles to B-particles. We report our results in dimensionless LJ units. The system was equilibrated at different temperatures $T$ in the range (0.451,0.550). The density $\rho$ varied from 1.09 particles per unit volume at the highest temperature to 1.19 at the lowest $T$ simulated. For reference, the mode-coupling temperature $T_m$ for this system is $T_m = 0.435$ at $\rho \approx 1.20$. So all the simulation data analyzed here is well above the glass transition.

Configurational histories for up to $4 \cdot 10^6$ molecular dynamics time-steps following equilibration were stored for each run. Following equilibration in the NPT and NVT ensembles, the trajectories were calculated in an NVE ensemble, and snapshots containing the particle coordinates and velocities were taken at logarithmic time intervals during the run. In this stage, the equations of motion were integrated using the velocity Verlet algorithm with a step size of 0.0015 at the highest temperature, and 0.003 at all other temperatures. Adopting argon values for the LJ parameters of the large particles implies an observation time of $\approx 26$ ns for the coldest $T$. All data presented here are calculated for the majority (A) particles only, except where otherwise noted. Further details of the simulation can be found in Ref. 3.

![FIG. 2. Mean square displacement of the majority species (A particles) vs. time for different $T$.](image)

Over the temperature-density regime studied, the system exhibits the usual features of a fragile, glassforming liquid. For example, the mean square displacement $\langle r^2(t) \rangle \equiv \langle 1/N_A \sum_{i=1}^{N_A} |r_i(t) - r_i(0)|^2 \rangle$ for the A particles is shown in Fig. 2 for different $T$. Here $r_i(t)$ is the position of particle $i$ at time $t$, $N_A$ is the number of A particles (6400), and $\langle \cdot \rangle$ denotes an ensemble average. For each state point, a “plateau” exists in both the mean square displacement and the self-part of the intermediate scattering function $F_s(q,t)$ as a function of $t$ (see below). The plateau in Fig. 2 separates an early time “ballistic” regime from a late time diffusive regime. The plateau is interpreted as implying “caging” of the particles and this phenomenon is typical for liquids of low temperature or high density. Over the range of $T$ studied, the $\alpha$-relaxation time $\tau_\alpha$, describing the decay of $F_s(q,t)$ (at the value of $q$ corresponding to the first peak in the static structure factor), increases by 2.4 orders of magnitude, and follows a power law $\tau_\alpha \sim (T - T_c)^{-\gamma}$, with $T_c \approx 0.435$ and $\gamma \approx 2.8$. The simulated liquid states analyzed here therefore exhibit relaxation behavior characteristic of a
supercooled liquid. No long range structural correlations due to density or composition fluctuations are apparent in the simulation data.

III. CHARACTERISTIC DECORRELATION TIME AND SPACE SCALES

In Fig. 3 we show the MFPT $\tau(\epsilon)$ plot for six different runs corresponding to varying the temperature of the system from $T = 0.550$ to $T = 0.451$. In the inset we show the dynamic entropy $S(\epsilon) \equiv 1/\tau(\epsilon)$. Note that the variation of $\tau(\epsilon)$ with $\epsilon$ exhibits similar qualitative trends to the variation of $t$ with $\langle r^2(t) \rangle$ shown in Fig. 2.

For small $\epsilon$, corresponding to the inertial regime, $S(\epsilon)$ is insensitive to temperature. At intermediate $\epsilon$ values we see a decrease of $S(\epsilon)$ with decreasing $T$ and an increase in the magnitude of the slope in the log-log plot. A strong temperature dependence of $S(\epsilon)$ is apparent at a scale on the order of one interparticle distance ($\epsilon = 1$). On these larger scales, we show in a later subsection that $S(\epsilon)$ exhibits a power-law scaling with $\epsilon$ and reduced temperature.

It is apparent from Fig. 2 that the particle displacement in this cooled liquid is not Brownian over most of the simulation time scales, and it is conventional to quantify this deviation by a “non-Gaussian parameter” $\alpha(t)$ involving the moments $\langle r^2(t) \rangle$ and $\langle r^4(t) \rangle$ of the self part of the van Hove correlation function $G_s(r,t) \equiv \langle \frac{1}{N_A} \sum_{i=1}^{N_A} \delta(r - (r_i(t) - r_i(0))) \rangle$. The parameter $\alpha(t)$ is defined as,

$$\alpha(t) = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1,$$

and vanishes for Brownian motion. $\alpha(t)$ is shown in Fig. 4 together with $\tau(\epsilon)$ for the coldest run ($T = 0.451$); note that for $\alpha(t)$, time $t$ is plotted on the ordinate axis. This comparison allows us to identify four regimes: An inertial regime (Regime I) where the non-Gaussian parameter is small; a “localization” regime characterized by a large value for the slope in the $\tau(\epsilon)$ log-log plot and by a growing $\alpha(t)$ (Regime II); a regime of particle motion that is persistent relative to Brownian motion, and where $\alpha(t)$ decreases (Regime III); and a fourth regime where the non-Gaussian parameter has decayed back to very small values so that the particle motion is nearly Brownian (Regime IV). The four regimes are examined in detail in the following subsections.

We emphasize that while some parallelism exists between the mean square displacement and the first-passage time, the inset of Fig. 3 comparing these quantities shows that they are not equivalent. However, if the distribution of particle displacements $G_s(r,t)$ were always exactly Gaussian (i.e. $\alpha(t) = 0$ for every $t$), then a simple inverse function relation should hold between these quantities. $G_s(r,t)$ obeys a “scaling relation” if we can rescale $G_s(r,t)$ as,

$$G_s(r,t) = \frac{1}{t^\nu} f \left( \frac{r}{t^\nu} \right),$$

where $f$ is some function. Simple dimensional analysis based on (3.2) implies,

$$\langle r^2(t) \rangle \propto t^{2\nu}$$

FIG. 3. Mean first-passage time $\tau$ of the majority species (A particles) versus $\epsilon$, for different $T$. Inset: Mean first-passage time dynamic entropy $S(\epsilon)$. Compare the $S(\epsilon)$ variation observed here for a cooled liquid with the dynamic entropy $h(\epsilon)$ calculated for a one-dimensional model map exhibiting diffusion at long times (see Fig. 25b of Gaspard and Wang [8]).

FIG. 4. Classification of dynamic regimes. MFPT $\tau(\epsilon)$ (solid curve) plotted versus $\epsilon$, and the non-Gaussian parameter $\alpha(t)$ (dashed curve) plotted versus $t$, for $T = 0.451$. Inset: Comparison between $\tau(\epsilon)$ (solid curve) and $\langle r^2(t) \rangle$ (dot-dashed curve) on a linear scale.

FIG. 4. Classification of dynamic regimes. MFPT $\tau(\epsilon)$ (solid curve) plotted versus $\epsilon$, and the non-Gaussian parameter $\alpha(t)$ (dashed curve) plotted versus $t$, for $T = 0.451$. Inset: Comparison between $\tau(\epsilon)$ (solid curve) and $\langle r^2(t) \rangle$ (dot-dashed curve) on a linear scale.
and the scaling of the first-passage time with \( \epsilon \),
\[
\tau(\epsilon) \propto \epsilon^{1/\nu}.
\]

In practice, these idealized scaling relations are restricted to certain time and space scales. Scaling with \( \nu = 1 \) is observed in the short time inertial regime. This result can be inferred from the general relation between the second moment of \( G_s(r, t) \) and the particle velocity,
\[
\langle \mathbf{r}(0) \cdot \mathbf{r}(t) \rangle = \frac{1}{2} \frac{d^2 \langle r^2(t) \rangle}{dt^2},
\]
and the constancy of the velocity autocorrelation function at short times [42, 43].
\[
\langle \mathbf{r}(0) \cdot \mathbf{r}(t) \rangle \rightarrow \langle \mathbf{r}(0) \cdot \mathbf{r}(0) \rangle \equiv v_o^2 \quad t \rightarrow 0,
\]
where \( v_o \) is the average particle velocity. Integrating Eq. 3.5 over a short time interval obviously gives \( \langle r^2(t) \rangle \sim t^2 \) or “ballistic-like” motion. Actually, this scaling is just a consequence of the existence of equilibrium, and should not be construed as necessarily implying the absence of interparticle interactions at short timescales [43]. A Gaussian form for the van Hove correlation function in this short time regime is ensured by the Maxwell-Boltzmann distribution for the particle velocities. In the opposite extreme of very long times, the central limit theorem governing the sum of independent particle displacements implies that the particle displacement distribution is Gaussian, and that \( \nu = 1/2 \). Transient scaling regimes can be observed at intermediate time scales, however. We refer to particle displacements as “persistent” relative to Brownian motion if \( \nu > 1/2 \), or “localized” relative to Brownian motion if \( \nu < 1/2 \).

### A. Inertial regime

In the limit of very small \( \epsilon \) we probe the fast microscopic dynamics associated with the decorrelation of the particle momenta. It is difficult to probe this decorrelation directly using the first-passage time approximation to the dynamic entropy. Fig. 3 indicates that our approximation for the dynamic entropy appears to diverge for \( \epsilon \rightarrow 0 \), so our approximation must break down in this limit. Gaspard and Wang have pointed out before that the first-passage time approximation to the dynamic entropy breaks down in this limit [13], so this shortcoming is to be expected. An estimate of the expected plateau in \( S(\epsilon) \) corresponding to the Kolmogorov-Sinai entropy can be obtained by determining a cut-off time of the first-passage time distributions in the fast dynamics regime.

The dynamics in this regime is examined by setting the magnitude of the first-passage sphere (\( \epsilon \)-sphere) about the center of each particle to be small enough that a collision does not usually occur before the particle leaves the \( \epsilon \)-sphere (see Fig. 1). By focusing on the particle first-passage time in this regime we identify a time and space scale over which particle velocities begin decorrelating. The first-passage time in this regime is insensitive to the type (A or B) of particle since they have the same mass. This is apparent in Fig. 5 where the first-passage time distributions for both the A and B particles at \( T=0.451 \) and \( \epsilon = 0.1 \) for \( T=0.468 \). Inset: log-log plot of the same data. Note that the asymptotic linear scaling of \( \tau(\epsilon) = 1.14\epsilon \) (solid lines) breaks down around a value \( \epsilon_v \approx 0.05 \), corresponding to \( \tau_v \approx 0.6 \). \( \epsilon_v \) and \( \tau_v \) are approximately independent of temperature (see also Fig. 3).

The idealization of ballistic particle motion implies the time \( \tau(\epsilon) \) it takes for the particle to exit the sphere of radius \( \epsilon \) equals \( \epsilon / v_0 \). Fig 6 shows an expanded plot of \( \tau \)
versus $\epsilon$ in the small $\epsilon$ regime where this linear dependence of $\tau$ on $\epsilon$ is apparent. A non-linear dependence of $\tau$ on $\epsilon$ develops as the particle velocities decorrelate at a “velocity decorrelation scale” $\epsilon_v \approx 0.05$. This distance corresponds to the time $\tau_v \approx 0.6$ (on the order of $10^{-13}$ s in argon units). We find that $\epsilon_v$ and $\tau_v$ are approximately independent of temperature in the present simulation (see also Fig. 3).

The first-passage time distributions $P_t(t)$ in the inertial regime. Main figure contains six different temperatures at $\epsilon = 0.1$ plotted log-log. Solid line indicates Eq. 3.7 where the constant of proportionality has been adjusted to best fit the data. The long-dashed line indicates the cut-off distribution function Eq. 3.8 with no free parameters. Inset: $P_t(t)$ at $T = 0.468$ for $\epsilon = 0.03$. This value of $\epsilon$ is less than the velocity decorrelation scale $\epsilon_v$ indicated in Fig. 6. Eqs. 3.7 and 3.8 are also shown in comparison with the simulation data. Note the absence of the long tail in the inset distribution.

We obtain further insight into the decorrelation of particle velocities in the inertial regime by examining the distribution of first-passage times, $P_t(t)$, as a function of $\epsilon$. Fig. 7 shows $P_t(t)$ for $\epsilon = 0.1$ and $\epsilon = 0.03$ for $T = 0.468$. We obtain a good approximation to $P_t(t)$ in the inertial regime through a Gaussian approximation for $G_s(r,t)$ [4] in conjunction with the first-passage distribution for Brownian paths [13]. The first-passage time distribution $P_t(t)$ scales as

$$P_t(t) \sim \exp \left( -\frac{\epsilon^2}{2(R^2)} \right)$$

(3.7)

at short times and decays exponentially at long times, $P_t(t) \sim \exp [-t/\tau(\epsilon)]$ [4]. We then introduce the approximation

$$P_t \simeq \frac{A}{t^2} \exp \left[ -\frac{1}{2} \left( \frac{\epsilon}{\nu_0 t} \right)^2 - \frac{t}{\tau(\epsilon)} \right]$$

(3.8)

where $A$ is a normalization constant. $(R^2)^{1/2}$ in Eq. 3.7 has been replaced by $\nu_e t$ based on the assumption that the particle displacements are nearly “ballistic” in the inertial regime. Note that the limiting expression for $P_t(t)$ given by Eq. 3.7 can also be deduced by assuming a Maxwell velocity distribution (one-dimensional due to the near rectilinear motion) with the velocity replaced by $\epsilon/t$. Fig. 7 shows that Eq. 3.7 (solid line) does not provide an accurate fit to the data using $\nu_0 = 1/1.14$ from the linear slope in Fig. 3, while the approximate expression Eq. 3.8 fits well for $\epsilon$ less than the “velocity decorrelation scale” $\epsilon_v \approx 0.05$. For $\epsilon > \epsilon_v$, $P_t(t)$ shows evidence of developing a power-law “tail” at long times, as seen in the main part of Fig. 7. This tendency becomes more developed at larger $\epsilon$, as discussed in the next subsection. The inset of Fig. 7 shows first-passage time data for $\epsilon < \epsilon_v$ where the tail is nearly absent and the cut-off is evident. At this point, we note that in liquids $h_{KS}$ characteristically scales as the inverse of the average interparticle collision time and thus has the interpretation of a microscopic “collision rate” [2,4]. The time $\tau_v$ can be considered as an average particle collision time so that an inverse relation between $h_{KS}$ and $\tau_v$ is expected. We do not consider the relation between $\tau_v$ and $h_{KS}$, since simulations over a broader temperature range and the direct calculation of the Kolmogorov-Sinai entropy through Lyapunov exponent spectra [11,17] are required for such an investigation.

B. Particle localization regime

The tendency of particle motion to become increasingly localized, as emphasized by the mode-coupling theory, is a conspicuous feature of experimental and simulation data on supercooled liquids. The “plateau” in the mean square displacement log-log plots (see Fig. 2) indicates transient particle localization or “caging”, and the persistence of this plateau increases with decreasing $T$ [4]. Next, we utilize the dynamic entropy concept to quantify this particle localization.

An increase in the slope of $\log(\tau(\epsilon))$ versus $\log \epsilon$ in Fig. 3 provides evidence for localization. A numerical differentiation of the data in Fig. 3 is shown in Fig. 8a where $\Delta(\epsilon)$ denotes the logarithmic derivative $\Delta(\epsilon) \equiv d\log \tau/d\log \epsilon$. The scaling behavior in Eq. 3.4 implies that $\Delta(\epsilon)$ corresponds to the fractal dimension $1/\nu$ of the particle trajectories. Fig. 8a shows that for all $T$, $\Delta(\epsilon) \to 1$ for small $\epsilon$, and $\Delta(\epsilon) \to 1/\nu$ for large $\epsilon$. At intermediate values of $\epsilon$, we observe that $\Delta(\epsilon)$ develops a maximum at $\epsilon_c$, corresponding to the inflection point in Fig. 3. This length scale defines a distance that is difficult for the particle to exceed, and thus we define $\epsilon_c$ as the “cage” size. The inset in Fig. 3b shows that $\epsilon_c$ decreases with temperature, so that increased particle confinement occurs with cooling.

Independent evidence indicating the significance of this characteristic scale is discussed later in this subsection.

We denote the value of $\Delta(\epsilon)$ at $\epsilon_c$ by the “localization parameter” $\Lambda(T) \equiv \max \Delta(\epsilon) = \Delta(\epsilon_c)$, and its
$T$-dependence is shown in Fig. 8b. The value of $\Lambda(T)$ increases with cooling, consistent with increasing particle localization ($\nu < 1/2$). The relatively noisy data in Fig. 8b can be fitted by a power law, $\Lambda(T) = 2 + 0.15(T - T_c)$ with $T_c = 0.435$.

Our identification of the cage size $\epsilon_c$ from the maximum value of $\Delta(\epsilon)$ is further supported by the examination of the first-passage time distribution $P_t(\epsilon)$ for $\epsilon$ near $\epsilon_c$. We find that $P_t(\epsilon)$ develops a long time power-law tail in this intermediate regime which is symptomatic of the development of intermittency in particle motion and particle localization [36]. In Fig. 9 we show for $T = 0.451$, $P_t(\epsilon)$ at several values of $\epsilon$ near $\epsilon_c = 0.21 \pm 0.02$. The apparent power law for the $P_t(\epsilon)$ tail varies with $\epsilon$ and has a value near 2 for $\epsilon \approx \epsilon_c$.

FIG. 8. (a) $\Delta(\epsilon) \equiv d \log \tau(\epsilon)/d \log \epsilon$ for (from top to bottom) $T = 0.451, 0.457, 0.468, 0.480, 0.505$, and 0.550. Inset: “Cage” size $\epsilon_c$ versus $T$. (b) $\Lambda \equiv \max \Delta(\epsilon)$ plotted versus $T$. The dashed line is a power law fit to the data as indicated in the text.

This power-law tail behavior in $P_c(t)$ is shared by the four coldest temperatures, as shown in Fig. 10, where the asymptotic behavior of the distributions is seen to be numerically very similar. The difference in their first moments [i.e. $\tau(\epsilon_c)$ in Fig. 3] reflects both the differences between the distributions in Fig. 10 at short times, and the asymptotic cut-off in the distributions that is difficult to resolve numerically.

FIG. 9. First-passage time distributions for $T = 0.451$, at different values of $\epsilon$ near $\epsilon_c = 0.21 \pm 0.02$. The dashed line indicates an inverse power law $t^{-2}$ for comparison.

FIG. 10. First-passage time distributions at the cage scale, $\epsilon = \epsilon_c$, for four different $T$.

Odagaki [36] has suggested that the second and first moments of the first-passage time distribution at the scale of one interparticle distance diverge at $T_c$ and at the glass transition temperature $T_g$, respectively, and a recent paper by Hiwatari and Muranaka [49] supports this glass transition scenario. A transition to intermittent particle motion at the glass transition has also been suggested by Douglas and Hubbard [37]. Our observations are consistent with the growth of intermittency of particle motion as $T_c$ is approached, but we cannot confirm theoretical predictions of a dynamical transition in the degree of intermittancy until lower temperatures are examined. An accurate test of these predictions will require carefully equilibrated data below $T_c$, beyond the
temperature range of the simulations analyzed here. We point out that, in the present system, the scale at which this intermittency occurs is substantially smaller than one interparticle spacing, and instead pertains to motion at the scale of the cage size, $\epsilon_c$.

C. Regime of persistent particle motion

Previous work has shown that particle motion becomes increasingly collective in this supercooled liquid and that an important mode of motion at the scale of the interparticle distance involves the string-like collective motion of particles. A visualization of this process [54] suggested to us that this process becomes increasingly “coherent” or “jump-like” at lower temperatures and this tendency towards “coherent jumping” has been noticed in a number of other physical systems (melting of hard disks [51], hexatic liquids [52] and ordering plasmas [53]). In this subsection we utilize $S(\epsilon)$ to further quantify this effect.

Regimes I and II were defined by characteristic spatial scales at which changes occur in the first-passage time distributions. However, the long run times of the simulations analyzed here necessitated the storing of configurations on a logarithmic, rather than linear, time scale, for all but the coldest simulation [58]. As a consequence, first-passage time distributions cannot be obtained over a continuous range of $\epsilon$ for large $\epsilon$. In the absence of this information, we roughly identify Regime III by the tendency for the non-Gaussian parameter $\alpha(t)$ to decrease (see Fig. 4). In Fig. 11 we show the apparent fractal dimension $\Delta(\epsilon)$ in Regime III for the highest and lowest temperatures. (The results for all $T$ are shown over an extended scale in Fig. 8). Notice that persistent particle motion ($\Delta(\epsilon) < 2$) develops for $\epsilon > 0.6$ in Fig. 8 (although $\Delta$ remains near 2 at the highest temperatures) and consequently we show $\Delta(\epsilon)$ for the range $0.7 < \epsilon < 1.0$ in Fig. 11. The value of $\epsilon$ at which $\Delta(\epsilon) = 2$ provides a more precise estimate for the beginning of Regime III. Although the data is noisy, we find that $\Delta(\epsilon) \approx 2$ within numerical error, and is nearly independent of $\epsilon$ for high $T$. Particle displacement at high temperature is then reasonably approximated by Brownian motion on these spatial scales. However, a substantially smaller average value of $\Delta(\epsilon) \approx 1.7$ (dashed line in Fig. 11) is found for the lowest $T$. Thus, we find the particle motion becomes increasingly persistent on cooling.

Why is persistent motion not observed in the mean square displacement? The tendency for persistent particle motion is not apparent in $\langle r^2(t) \rangle$ shown in Fig. 8 or in the inset of Fig. 10 because, when averaging over the squared displacements, the contribution of the few particles that are at any given time moving persistently is “washed out”. However, these particles give a large contribution to the mean first-passage time, so that this quantity is therefore a sensitive indicator of persistent particle motion.

![FIG. 11. Apparent fractal dimension $\Delta(\epsilon)$ of particle displacements in Regime III. From Fig. 8, highest and lowest simulation temperature $T = 0.5510$ and $T = 0.4510$ are shown for $0.7 < \epsilon < 1.0$.](image)

We can obtain insight into the emergence of persistent particle motion in our cooled liquid from idealized models of Brownian motion subject to potential fluctuations. If the potential fluctuations are quenched, there is a tendency towards particle localization [54], but the occurrence of fluctuations in the potential in both space and time can lead to persistent particle motion. In particular, if the fluctuations are delta-correlated in both space and time, then the exponent $\Delta$ equals 3/2 [55]. The effects observed in Ref. [55] are qualitatively consistent with our understanding of the origin of correlated motion. At short times, the existence of relatively immobile particles leads to a randomly fluctuating field felt by those particles free to move at a given point in time. This spatially fluctuating field is responsible for the particle caging or localization on timescales short compared to the decorrelation time $\tau_\alpha$ of the “structural fluctuations” (associated with the relatively immobile particles). At longer times, the formerly immobile particles become mobile and the potential field fluctuates in time, leading to an enhancement in the particle displacement. At still longer times, thermal fluctuations restore equilibrium and particle displacement ultimately becomes diffusive.

Finally, we point out that particle motion can be persistent even in the absence of a secondary (so-called “hopping”) peak in $G_s(r, t)$. Instead, persistent particle motion contributes to a long tail in $G_s(r, t)$ in the temperature range of the present system [54]. This long tail sharpens up and becomes a secondary peak at lower $T$ [56], indicating the increased contribution of collective particle motion to transport below $T_c$. 

8
D. Large scale particle displacement

Particle displacement in a liquid at large scales is described by Brownian motion so that $S(\epsilon)$ should scale asymptotically as $\epsilon^2$ for large $\epsilon$, regardless of temperature. It is apparent in Fig. 2 that the data in the asymptotic diffusive regime is limited, especially at lower temperatures. Previous work has shown that there is a limited regime of Brownian motion so that

\[ S = 1 \]

Thus, one interparticle distance is taken to be the minimal scale of the large scale particle displacement regime (Regime IV).

FIG. 12. Dynamic entropy at the scale of one interparticle separation, $S(\epsilon = 1)$, versus $T - T_c$, with $T_c = 0.435$. Diamonds refer to the simulation data for $S(\epsilon = 1)$, and the dashed lines refer to the power law, $S(T) \sim (T - T_c)^{2.5}$. We also observe this scaling for $S(\epsilon = 0.4)$ (circles). The inverse of the structural relaxation $1/\tau_\alpha$ (triangles) follows a power law $1/\tau_\alpha \sim (T - T_c)^{2.8}$. Inset: Schematic indication of expected temperature variation of dynamic entropy $h_{KS}$ at small scales. Note that the extrapolated ergodic-nonergodic transition in the $\epsilon \to 0$ limit should occur at a temperature $T_o < T_c$.

In the previous discussion, we have established that $S(\epsilon)$ is insensitive to temperature for small $\epsilon$ over the temperature range investigated. This insensitivity accords with the expected variation of dynamic entropy $h_{KS}$. At higher $T$ we expect the dynamic entropy to saturate, while a decrease should accompany the more restricted particle motion at lower $T$. A variation similar to that shown in the inset of Fig. 12 has been established for the ordering of the XY model. The investigation of the anticipated ergodic-nonergodic transition and its possible relation to a vanishing of $h_{KS}$ requires the calculation of the full Lyapunov spectrum, which is currently prohibitive for a system of the present size. However, we can investigate $S(\epsilon)$ at a larger scale on the order of an interparticle spacing. This should be interesting because of the strong $T$-dependence in $S(\epsilon)$ at this length scale noted above (see Fig. 3).

In Fig. 12 we examine the $T$-dependence of $S(T; \epsilon)$ at the scale of one interparticle separation $\epsilon = 1$. We observe that $S(T; \epsilon = 1)$ obeys a power law to a good approximation over the temperature range investigated, and that $S(T; \epsilon = 1)$ seems to extrapolate to zero at the mode-coupling temperature $T_c = 0.435$. As shown in Fig. 12, a reasonable fit to the data is obtained with the relation

\[ S(\epsilon = 1) \sim (T - T_c)^{2.5}, \quad T_c = 0.435. \]

The scaling of $S(T; \epsilon = 1)$ is compared in Fig. 12 to the structural relaxation time $\tau_\alpha$ describing the decay of the intermediate scattering function. Although the scaling of the two quantities is qualitatively similar, the best fit exponent for $\tau_\alpha$ has the somewhat larger value of $2.8$.

The power law scaling of $S(\epsilon = 1)$ with temperature is not obvious since if the particle displacement were exactly described by Brownian motion, then $\tau(\epsilon)$ would scale in inverse proportion to the diffusion coefficient. A determination of the diffusion coefficient for A particles is obtained by a simple least-squares fit (not shown) of the long time data to the function $\langle \tau^2(t) \rangle = A + 6Dt$. This fitting gives

\[ D \sim (T - T_c)^{2.1}. \]

A more refined estimate by Kob and Anderson on a smaller (1000 particles) system gave an exponent 2.0 for the A particles. The diffusion data thus scales with a fractional power of the structural relaxation time.
over the temperature range investigated. Since evidence
supports a common temperature scaling of $\tau_\alpha$ and the
fluid viscosity $\eta$ [52], the observation implied by Eq.
(3.11) is consistent with the breakdown of the Stokes-
Einstein relation in real and simulated supercooled li-
quids [60,61]. We therefore conclude that $S(\epsilon = 1)$ scales
neither exactly like the inverse structural relaxation time
$1/\tau_\alpha$ nor the diffusion coefficient $D$. Other characteristic
times exist for this liquid. It has recently been reported
for the same simulations investigated here that the time
scale on which particle displacements are most correlated
scales as a power law with $(T - 0.435)$, with an exponent
$\gamma = 2.3 \pm 0.2$ [6]. This exponent notably agrees within
numerical error with the exponent in Eq. (3.11). We further
note that the time $t^*$ at which $\alpha(t)$ is a maximum (see
Fig. 4) appears to diverge at $T_c$ with an exponent 1.7 [3].

Since the temperature dependence of $S(\epsilon)$ is largest in
Fig. 3 for $\epsilon = 1$ and very small for $\epsilon \to 0$, it is natu-
ral to consider the temperature dependence of $S(\epsilon)$ for
many fixed $\epsilon$ to determine how this crossover occurs. In
Fig. 13 we see that the scaling $S(T) \propto (T - T_c)^{2.5}$ holds
for $\epsilon$ greater than the cage size $\epsilon_c$ and sufficiently small
reduced temperature. We also find that for any temper-
ature, the scaling fails for $\epsilon < \epsilon_c$. This provides another
method for determining the cage size.

\[ D \sim \tau_\alpha^{-(2.1/2.8)} \simeq \tau_\alpha^{-0.75} \]

FIG. 13. Mean first-passage time $\tau(\epsilon)$ versus $T - T_c$, cal-
lculated at fixed values of $\epsilon$. Dotted lines denote the power law
$S(T) \sim (T - T_c)^{2.5}$.

IV. CONCLUSION

We have studied the length-scale dependence of the dy-
namic entropy $S(\epsilon)$ in a molecular dynamics simulation
of a model supercooled binary Lennard-Jones liquid. The
simulations were performed above both the glass transi-
tion temperature and the mode-coupling critical temper-
aturc and correspond to equilibrated liquid states [3].

$S(\epsilon)$ as estimated by the MFPT provides a tool for
identifying characteristic length and time scales of the
dynamics of liquids and provides a means for quantifying
the degree of correlated motion occurring in supercooled
liquids. At very small $\epsilon$ we observe a decorrelation of
particle velocity and an $S(\epsilon)$ which is insensitive to tem-
perature and $\epsilon$ variation. A decorrelation time associated
with an average interparticle collision time is identified.

At intermediate values of $\epsilon$ we observe a sharp drop in
$S(\epsilon)$ with increasing $\epsilon$, indicating that the path motion
is more “stochastic” at these length scales. $S(\epsilon)$ is found
to have a strong temperature dependence as well in this
regime. The logarithmic derivative $\Delta \equiv d \log \tau/d \log \epsilon$
becomes a maximum at a characteristic $\epsilon$ value that is
identified with the particle “cage” size $\epsilon_c$, since par-
icle localization is maximal at this point. The scaling of
$S(\epsilon)$ with temperature at fixed $\epsilon$ gives an independent
confirmation of our estimation of $\epsilon_c$ because it exhibits
a qualitatively different dependence on temperature for
$\epsilon > \epsilon_c$ and $\epsilon < \epsilon_c$. The localization parameter $\Delta \equiv \Delta(\epsilon_c)$
increases and the cage size $\epsilon_c$ decreases as the liquid is
cooled. The distribution functions for the first-passage
time at the scale of the cage size, $P_c(t)$, in the coldest
runs exhibit a long power-law tail, consistent with sugges-
tions that there is growing intermittency in the particle
displacements in glass-forming liquids [66,67]. This fea-
ture requires further study in cooler liquids to check the
predictions of these models. At still larger scales (still
less than one interparticle separation) we observe persis-
tent motion which follows the transient particle “caging”.

$S(\epsilon)$ obeys a power law $S(\epsilon) \sim \epsilon^{-1/\nu}$ for $\epsilon$ in the range
$(0.7, 1)$ where the apparent fractal dimension of the par-
icle trajectories $D(\epsilon) = 1/\nu$ ranges from $\approx 2$ to $\approx 1.7$
as the temperature is lowered. Thus, we observe a ten-
dency for the particle motion to acquire a persistent char-
acter relative to Brownian motion as it is cooled. This
is consistent with the previous observation of correlated
string-like motion in this liquid [3].

General arguments suggest that the dynamic entropy
at microscopic scales decreases at low temperatures, but
a slower variation should be obtained at higher temper-
atures, as in the present molecular dynamics calculation
(see Fig. 2). The situation is not so clear for the first-
passage time dynamic entropy $S(\epsilon)$ at the scale of one
interparticle separation $\epsilon = 1$. In this case $S(\epsilon = 1)$ is
inverse to the “average interparticle exchange time $\tau(1)$”,
$\epsilon(1)$. We find that $S(\epsilon)$ vanishes as a power law,
$S(\epsilon = 1) \propto (T - T_c)^{2.5}$, when the mode-coupling
temperature $T_c$ is approached from above. Thus, the cooled
liquid has the appearance of approaching an ergodic
non-ergodic transition as $T \to T_c$, when viewed at the
scale $\epsilon = 1$. This is consistent with the predictions of
mode-coupling theory.

The first-passage time can also be utilized to obtain in-
formation about the spatial dependence of mobility fluctu-
ations in cooled liquids. Perera and Harrowell [63] for
example, have examined the position dependence of $\tau$ at the scale of one interparticle spacing in a two-dimensional soft-sphere supercooled liquid and found a tendency for particles of relatively high and low “mobility” (i.e., small and large $\tau$, respectively) to cluster as $T$ is lowered. A detailed study of spatial correlations of first-passage times in the present system will be presented elsewhere.\[24\]

Future work should examine our approximate expression for $S(\epsilon)$ in the $\epsilon \to 0$ limit through independent calculation of the Kolmogorov-Sinai dynamic entropy, $S(\epsilon \to 0) \equiv h_{KS}$. The temperature dependence of $h_{KS}$ in cooler liquids ($T < T_c$) should be examined to determine if there is a tendency for the “bare” dynamic entropy to vanish at a lower glass transition temperature (see inset of Fig. 12). Recent work has established a phenomenological relation between entropy $h_{KS}$ and the equilibrium entropy in simulations of model liquids at relatively elevated temperatures $\[14\]$. A decrease in $h_{KS}$ at lower $T$ should be accompanied by the development of collective motion at short times. Such motion has been reported in Ref. $\[49\]$. We expect this change in the short time dynamics to be relevant for interpreting the Boson peak phenomenon in cooled liquids $\[55\]$. Simulations have already shown that the fraction of unstable modes $f_u$ in a cooled liquid decreases in parallel with $h_{KS} \[24\]$, and the vanishing of $f_u$ has been identified with the temperature where the diffusion coefficient $D$ vanishes $\[66,67\]$. Finally, we note that the calculation for $S(\epsilon)$ can be extended to other dynamical variables associated with other transport properties (viscosity, thermal conductivity, etc.) and these calculations should provide useful estimates of other characteristic space and time scale in cooled liquids $\[18\]$. We emphasize that although the definition of $S(\epsilon)$ is motivated by dynamical systems theory concepts, this quantity defines an independently interesting measure of correlated motion in liquids that does not rely on the approximation relating $S(\epsilon)$ to $h(\epsilon)$.

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