

Calculating the hopping rate for self-diffusion on rough potential energy surfaces: Cage correlations

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We present a method for estimating the hopping rate for Zwanzig's model of self-diffusion in liquids [R. Zwanzig, *J. Chem. Phys.* **79**, 4507 (1983)]. To obtain this estimate, we introduce the cage correlation function which measures the rate of change of atomic surroundings, and associate the long-time decay of this function with the basin hopping rate for diffusion. Results from a set of simulations on Lennard-Jones particles are presented. A simple analytic model for the diffusion constant in supercooled and normal liquids that is based on estimates of the activation energy obtained via the cage correlation function is derived. We discuss the breakdown of Zwanzig's hopping mechanism for mass transport as well as the low temperature behavior of the self-diffusion constant on rough potential energy surfaces. © 1997 American Institute of Physics. [S0021-9606(97)52241-0]

I. INTRODUCTION

The theory described herein builds on Stillinger and Weber's¹⁻⁴ inherent structure theory for liquids. The idea behind inherent structure theory is that there is a division between the vibrational dynamics of liquids and the large-scale structural changes that happen over a much longer time scale. Earlier approaches that bear some similarity to this idea can be found in Eyring's method of significant structures⁵ and in some studies of pair-correlation functions from the time-averaged particle positions in water simulations.^{6,7} Stillinger and Weber's contribution was the mapping of the atomic positions throughout the simulation onto a sequence of local minima on the potential energy surface. The mapping was made by following the steepest descent path (or *quenching*) to the nearest local minimum. The many-body configuration space was thus divided into regions (or "cells") surrounding each local minimum. Over time, the liquid's configuration vibrates around a single local minimum, and occasionally hops to an adjacent minimum on the surface. The distribution of the inherent local minima depends on the temperature, density and on the topology of the potential energy surface.

In the solid, the inherent structure is identical to the crystal structure, and the vibrations are simply the phonons of the solid. In liquids, the inherent structures are metastable, and transitions between two different structures happen with some regularity. Stillinger and Weber observed that as their simulations progressed, the quenched configurations were stable for short periods of time and then suddenly jumped (with some recrossing) to other configurations.²

Based on the work of Stillinger and Weber, Zwanzig has suggested a model that relates self-diffusion to the longitudinal and shear viscosities in liquids.⁸ Zwanzig divides the configuration space into "cells," each associated with a local minima on the potential energy surface. One of the cells corresponds to the crystalline configuration and others to amorphous, or liquid-like configurations.

For a period of time, the liquid's configuration oscillates harmonically in one of these cells. Occasionally, the liquid configuration will have enough kinetic energy to cross a saddle point on the potential energy surface and will jump to the cell surrounding a different local minimum. The major effect of the jump between the cells is to rearrange the positions of some of the molecules. The positions of the remaining molecules are unchanged. The velocities of the particles before the jump is understood to be uncorrelated from the velocities after the jump.

The starting point in Zwanzig's theory is the Green-Kubo formula^{9,10} for the self-diffusion constant,

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle, \quad (1)$$

where $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ is the time-dependent velocity autocorrelation function. Zwanzig's model predicts the diffusion constant using τ , the lifetime which characterizes the distribution ($\exp(-t/\tau)$) of residence times in the cells.

Following a jump, the coherence of the harmonic oscillations is disrupted, so all correlations between velocities will be destroyed after each jump. Zwanzig writes the velocity autocorrelation function in terms of the velocities of the normal modes in the nearest cell. The normal mode frequencies are characterized by the normalized distribution function $\rho_q(\omega)$, and the time integral can be solved assuming the time dependence of a damped harmonic oscillator for each of the normal modes. In the continuum limit of normal mode frequencies, one obtains

$$D = \frac{kT}{M} \int_0^\infty d\omega \rho_q(\omega) \frac{\tau}{(1 + \omega^2 \tau^2)}, \quad (2)$$

where M is the mass of the particles.

Zwanzig does not explicitly derive the inherent structure normal modes from the potential energy surface (he used the Debye spectrum for $\rho_q(\omega)$ and estimated τ from the longitudinal and shear viscosities of the liquid). Moreover, the

theory avoids the problem of how to estimate the lifetime τ for cell jumps that destroy the coherent oscillations in the subvolume. Nevertheless, the model fits the experimental results quite well for the self-diffusion of tetramethylsilane (TMS) and benzene over large ranges in temperature.^{11,12}

Recently, Cao and Voth have provided a mathematical procedure which obtains the vibrational modes of the inherent structures. Their method is based on the optimized quadratic approximation,^{13–15} which allows them to transform the many-body potential energy surface into an effective quadratic potential. In their work, Cao and Voth introduce a universal decay function (similar to the one used by Zwanzig) which characterizes the metastable nature of the set of inherent structure normal modes. Cao and Voth provide some of the missing elements in Zwanzig model, but their approach does not provide a way to compute the universal decay function for an arbitrary system—indeed the lifetime τ is adjusted until they obtain the experimental self-diffusion constant.

Only one approach to calculating τ directly from molecular dynamics simulations has been presented in the literature (although the method could apply to Monte Carlo simulations as well). Keyes and co-workers have used instantaneous normal modes (INMs) (Ref. 16) in an attempt to compute the lifetime τ from first principles.^{17–21} Their primary contribution was an estimate for τ based on the unstable branch of the instantaneous normal mode density of states. In their theory, the potential energy surface of the system is expanded in a Taylor series (retaining terms up to quadratic order) around a set of instantaneous liquid configurations. The instantaneous normal modes frequencies are obtained by diagonalizing the force constant matrix at each of these configurations. The density of states for the INMs is then obtained by averaging over different liquid configurations. Since the liquid configurations are chosen from trajectories which have non-zero temperature, they will not necessarily be found at a minimum on the potential energy surface. Therefore, the density of states of the INMs exhibits both real and imaginary frequencies.

Keyes uses this density of states to obtain the distribution of barrier heights on the potential energy surface—barrier heights that he associates with the barriers between adjacent local minima on the potential energy surface. Most importantly, Keyes assumes that these barriers are the same barriers between the cells used in Zwanzig's theory. Keyes then estimates the hopping rate out of a given local minimum using transition state theory. The average rate is estimated by summing the transition state theory rate over all exit channels from a single minimum and averaging over all local minima on the surface. Readers interested in the details of this theory are urged to consult Ref. 19.

Recent work by other groups^{22–24} has attempted to correct some problems with the INM approach. The imaginary frequency INMs include contributions from non-barrier anharmonicities, and the corrections to the INM theory for diffusion have all centered around removing these non-barrier anharmonicities from the INM density of states. Bembenek and Laird followed projections along each INM and classi-

fied the modes into “double well” modes and “shouldered” modes.^{23,24} A projection along a double well mode will exhibit local minima on both sides of the instantaneous configuration, while a projection along a shouldered mode will exhibit only one local minimum along that direction. Bembenek and Laird further classify the double well INMs into “localized” and “extended” modes depending on how many atoms are involved in a mode's projected motion, and were able to study the kinds of motion that occur both above and below the glass transition temperature (T_g). Keyes has suggested that one should include in the density of states used to calculate τ only the double well or extended double well modes,²⁵ citing as evidence the fact that these modes disappear below T_g .²⁴

Vijayadamodar and Nitzan included only those modes in the density of states which have *zero-force*.²² Zero-force modes exist only when the configuration is very close to an extremum along that INM coordinate.

In a previous paper,²⁶ we have shown that one of the underlying assumptions of the INM theories is invalid—namely that the barriers observed in the INM theories really do correspond to diffusive barrier crossings. Lennard-Jones systems exhibit “false-barriers” in the INM picture. False barriers are imaginary frequency INMs which are accepted by both the double-well^{23,24} and zero-force²² modifications to the INM theory, but which quench to the same minimum from *both sides* of the barrier. These motions cannot be diffusive, but are included in the calculation of τ in all of the INM theories presented in the literature. This leads to an unphysically large estimate of the diffusion constant in the crystalline solids.

To our knowledge, no one has yet tested the limits of the Zwanzig model or reported a method for calculating the lifetime τ *correctly* from molecular dynamics simulations. This then is the aim of this paper—we seek a method to compute the lifetime τ and the survival distribution for cell jumps $f(t)$ (the universal decay function) and to establish the validity of the cell-hopping mechanism.

In Sec. II we present a model for self-diffusion, which is based on correlations between an atom's surroundings at different times. Based on the multiple time scales for changes in atomic surroundings, we posit a simple kinetic mechanism for self-diffusion by associating the slow time scale with hopping between basins, which can have many local minima on a rough potential energy surface. In Sec. III, we test the validity of the model over a wide range of temperatures and densities for liquid and solid argon, and compare our results to diffusion constants calculated via the Einstein relation⁹

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle, \quad (3)$$

where $\mathbf{r}_i(t)$ is the position of particle i at time t . We derive an approximate expression for the self-diffusion constant in Sec. IV, and discuss the temperature dependence of the approximate expression near the glass transition temperature (T_g). Section V concludes.

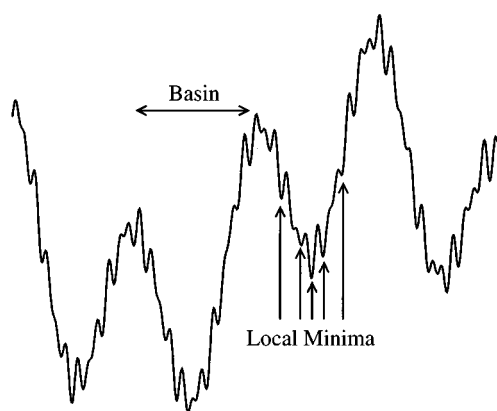


FIG. 1. A sketch of a "rough" potential energy surface which has a distribution of small barriers (with barrier heights characterized by E_{small}) superimposed on the real barriers to diffusion (characterized by E_{large}) which separate the basins from one another.

II. MODELING THE CHANGE IN ATOMIC SURROUNDINGS

Although we believe that the idea behind the Zwanzig cell-hopping model is correct, calculating τ by measuring changes in the potential energy of the quenched configurations² is probably not the best way to proceed. Since the N individual atoms may hop at any time in low-density liquids, hops to new local minima on the *global* potential energy surface happen at nearly every time step. This is a sign that the potential energy surface is "rough," i.e. there are very many small perturbing barriers superimposed on the background potential of large basins. Quenches to different local minima on a rough potential energy surface are not indicators of diffusive barrier hopping, since there can be many local minima within each basin. We cannot, therefore, use jumps in the quenched trajectories to obtain estimates for the hopping rates in the low-density liquids. A sketch of a rough one-dimensional potential surface is shown in Fig. 1.

Additionally, quenching to the nearest local minimum may cause many atoms to adjust their positions during the quench. Since a barrier crossing is involved, the quenched positions may be quite distant from the same positions in a previous quench, even though the atoms have not changed position by very much in the real trajectory. Therefore, measuring positional changes in the quenched trajectories can make it appear that more atoms are involved in a basin-hopping than would be the case in the real trajectory.

We have also seen that attempts to use local information (the INMs) on the potential energy surface can misidentify regions of negative curvature as the true barriers to diffusion, giving estimates of hopping times in the crystalline solids that are unphysically large.²⁶ This "false-barrier" problem persists into the liquid phase, and can give estimates of the hopping times that are inaccurate in that regime.

When an atom makes a jump to a new basin, the most striking change that occurs from the atom's point of view is that the surrounding atoms have suddenly changed. What we would like to be able to measure is exactly this—how often

do these changes in atomic surroundings take place? We would also like to be able to answer some questions about the basin-hopping process: How many atoms are involved in the hopping? How often does an atom return to its original surroundings?

To answer these questions, we have formulated a new correlation function that is an accurate measure of changes in the atom's surroundings. We first introduce the correlation function, and observe its time behavior in Lennard-Jones liquids and solids. Then we present a simple kinetic mechanism for diffusion based on observations made here and in previous work.²⁶ In Sec. III we will use this kinetic model to predict diffusion constants in Lennard-Jones liquids and solids over a wide range of temperatures and densities.

A. Generalized neighbor lists and correlation functions

An atom's immediate surroundings are best described as the nearest neighbors (in solids) or as the first solvation shell (in liquids). When a diffusion event has taken place, the atom has left its current solvation shell and entered a void (in solids, this could be an interstitial site or a vacancy²⁷) which has a different group of atoms surrounding it. If one were able to paint identifying numbers on each of the atoms in a simulation, and kept track of the list of numbers that each atom could see at any time, then the diffusion event would be evident as a substantial change in this list of neighbors. This is precisely what is done when using neighbor lists in molecular dynamics simulations—where they are used to reduce the time spent on computing interatomic forces. Traditionally, the list of nearby atoms is updated every few time steps, and the forces are calculated using only those atoms that are within each atom's list of neighbors. This can save an immense amount of CPU time, and has become an invaluable technique in large simulations.²⁸

A generalized neighbor list ($\mathcal{L}_i$) for atom i in an N atom system is a vector of length N , and is defined as

$$\mathcal{L}_i \equiv \begin{pmatrix} f(r_{i1}) \\ \vdots \\ f(r_{iN}) \end{pmatrix}, \quad (4)$$

where $f(r_{ij})$ is a function of the inter-atomic distance (r_{ij}). In large simulations, $f(r_{ij})$ is typically the Heaviside function,

$$f(r_{ij}) = \Theta(r_{n\text{list}} - r_{ij}) = \begin{cases} 1 & \text{if } r_{ij} \leq r_{n\text{list}} \\ 0 & \text{otherwise} \end{cases}, \quad (5)$$

where $r_{n\text{list}}$ is the neighbor list cutoff radius.

A radial cutoff is certainly not the only conceivable way of choosing the members of the neighbor list. An even more general neighbor list could depend on a complicated function of all of the atomic positions—the members of the $\mathcal{L}_i$ could be chosen as the 12 atoms that are closest to atom i , or one could use the number of faces of the Voronoi polyhedra^{29–31} to decide which atoms make up the surrounding cage. Both of these methods require a substantial amount of computational effort— $N^2 \log(N)$ operations for the sorting required

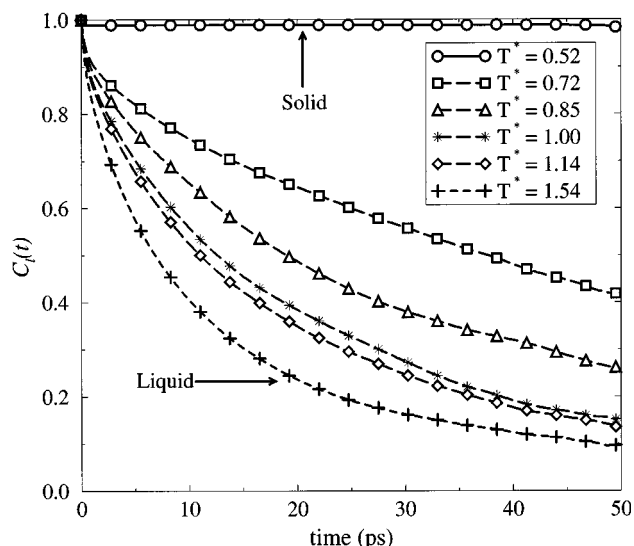


FIG. 2. A plot of the time-dependence of the neighbor list correlation function ($C_i(t)$) in solid argon, and in normal and supercooled liquid argon. The densities of all six simulations were $\rho^* = 0.94$. The solid simulation is shown with a solid line. Supercooled liquids are shown with dashed lines, and the liquid simulation is shown with a dotted line. Note the length of time it takes for the neighbor list correlation function to decay.

for the fixed-size neighbor lists and $N^3 \log(N)$ operations for the Voronoi polyhedra. The radial-cutoff neighbor list can be calculated during the simulation with a trivial amount of additional computational work.

We have chosen r_{list} differently than how one would choose it to speed the calculation of forces. In calculating $\mathcal{C}_i$, we set r_{list} to the location of the first minimum in the pair correlation function,²⁸

$$g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle, \quad (6)$$

which restricts our view of the atom's surroundings to those within the first solvation shell. This distance is not necessarily the best choice for r_{list} , but it provides a starting point for the calculation of neighbor list correlation functions.

We have discovered that there are some quite striking properties of correlation function,

$$C_i(t) \equiv \frac{\langle \mathcal{C}_i(0) \cdot \mathcal{C}_i(t) \rangle}{\langle \mathcal{C}_i(0)^2 \rangle}, \quad (7)$$

for the radial cutoff neighbor lists. In Fig. 2 we show the time dependence of $C_i(t)$ for some normal and supercooled liquids. Since the surroundings have to change completely for the correlation to drop to zero, the long-time decay of this function is extremely slow.

When an atom jumps to an adjacent cage, many of the original members of that atom's neighbor list persist into the atom's new neighbor list. What we seek is a correlation function that is a measure of whether or not the cage has undergone *any* real change in time t . To compute this, we must first know the number of atoms that have left or entered the neighbor list since the original configuration. The number of atoms that have left atom i 's original neighbor list at time t is

$$n_i^{\text{out}}(0, t) = |\mathcal{C}_i(0)|^2 - \mathcal{C}_i(0) \cdot \mathcal{C}_i(t), \quad (8)$$

while the number of atoms that have entered the neighbor list in that time is

$$n_i^{\text{in}}(0, t) = |\mathcal{C}_i(t)|^2 - \mathcal{C}_i(0) \cdot \mathcal{C}_i(t). \quad (9)$$

In these equations, $|\mathcal{C}_i(t)|^2$ is the number of atoms in i 's neighbor list at time t , while $\mathcal{C}_i(0) \cdot \mathcal{C}_i(t)$ is the number of atoms that are in i 's neighbor list at both time 0 and time t . One can deduce $n_i^{\text{in}}(0, t)$ easily from Eq. (8) by going backwards in time. The number of atoms leaving a list in a time-reversed simulation is identical to the number entering the list in a simulation run forward in time.

Next, we define c , which is the number of atoms that must leave or enter an atom's neighbor list before we can be reasonably sure that a change in surroundings has taken place. The correlation function for the cage is then

$$C_{\text{cage}}^{\text{in-out}}(t) \equiv \langle \Theta(c - n_i^{\text{out}}(0, t)) \Theta(c - n_i^{\text{in}}(0, t)) \rangle, \quad (10)$$

where Θ is again the Heaviside function. An alternative to this formula for $C_{\text{cage}}(t)$ is

$$C_{\text{cage}}^{\text{out}}(t) \equiv \langle \Theta(c - n_i^{\text{out}}(0, t)) \rangle. \quad (11)$$

This second form of the cage correlation function prevents us from counting too many of the vibrational motions of the cage atoms as changes in the composition of the cage. (Luzar and Chandler have introduced a concept similar to the cage correlation function in their study of the dynamics of hydrogen bonding between dimethyl sulfoxide (DMSO) and water,³² although in a less general form than what is introduced here.)

We have chosen $C_{\text{cage}}(t)$ from Eq. (11) and $c=1$ for most of the calculations in this paper. Logarithmic plots of the cage correlation function (out-only, $c=1$) for two densities are shown in Fig. 3. Since single atoms can leave and rejoin the neighbor list during normal vibrational motion, there is a significant decay of $C_{\text{cage}}(t)$ at short times. For solids, changes in the cage correlation function are due only to this vibrational motion. (This is true only for the relatively short time scale of the simulation. At much longer times atoms may diffuse, although the diffusion constant is many orders of magnitude smaller than in the liquids.) In the cage correlation function, the effect of vibrational motion is seen as a fast decay to a plateau (solid lines in Fig. 3). We refer to this fast decay as the "vibrational" decay channel. The value of $C_{\text{cage}}(t)$ at the plateau represents the average cage correlation, and is typically lower than one (in the logarithmic plots the value is lower than $0 = \ln(1)$). When the temperature is very low, the amplitude of the vibrations is insufficient to make any changes in the neighbor list. This explains why we observe the plateau value to be inversely proportional to the temperature and directly proportional to the density of the solids.

The situation in supercooled and regular liquids is somewhat more complex than in the solids. Two competing channels contribute to the decay of the cage correlation function. In addition to the vibrational channel, the cage can change when an atom hops over a barrier to an adjacent basin. It is

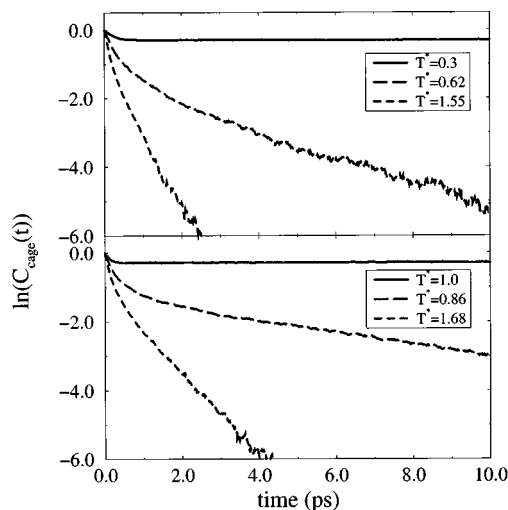


FIG. 3. A logarithmic plot of the time-dependence of the cage correlation function (Eq. (11)) for two different densities. The upper and lower panels are for reduced densities $\rho^* = \rho\sigma^3$ of 0.85 and 1.0 respectively. In each panel, the solid line is for the solid, the dashed line is for the supercooled liquid, and the dotted line is for a liquid that is well above the melting temperature. Note the clear separation of time scales between the vibrational and hopping decay channels in the supercooled liquids.

this hopping channel which is associated with the diffusion process. The long-time decay of $C_{\text{cage}}(t)$ in the liquids is therefore quite different than in the solids—the fast component is followed by a slower decay.

The decay of correlation functions over multiple time scales is by no means a newly-observed phenomenon. In the late 1970's, Chandler, Montgomery, and Berne^{33,34} observed this phenomenon in the correlation function for fluctuations in the number of particles at the barrier to isomerization of a model double-well system. They treated the dynamics using the reactive flux method,^{33–36} which has often been used to study rare events in liquids.³⁷

In the reactive flux method, the instantaneous rate of a process is equal to the first time derivative of the correlation function

$$k(t) = -\frac{dC(t)}{dt}. \quad (12)$$

At $t=0$, $k(t)$ will be exactly the transition state theory (TST) rate, but at short times, $k(t)$ will show deviations from the TST rate due to recrossings of the barrier. If there is a substantial separation of time scales between the fast recrossing process and the slow activation process, then $k(t)$ appears to stabilize to a plateau region at intermediate times. One can extrapolate the plateau values back to $t=0$ and can estimate the rate for the process from the intercept.³³

Since the atoms in our simulations also have many recrossings from one cage to another we expect a fast *non-exponential* relaxation followed by a slow *exponential* decay in the correlation function, which is exactly the behavior we observe in $C_{\text{cage}}(t)$. We do not, however, have the large separation of time scales that is required for the reactive flux method. Instead of extrapolating the plateau region in the

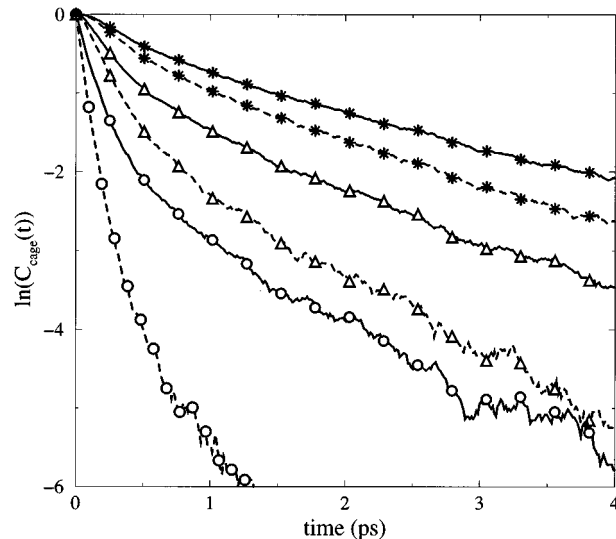


FIG. 4. A logarithmic plot of the time-dependence of the two formulations of the cage correlation function (Eqs. (10) and (11)) for different values of c . The solid lines are for the cage correlation function which uses only atoms that are leaving the neighbor list, while the dashed lines treat both entering and leaving atoms as changes in the cage. The symbols denote the different values of c . Open circles ($\circ$), triangles ($\triangle$), and stars ($\star$) are for $c=1, 2$, and 3 respectively.

derivative of the correlation function, we use a linear fit to the long-time decay of $\ln(C_{\text{cage}}(t))$ to obtain the rate.³⁸

Zwanzig's dynamical picture makes sense only if the amount of time spent in each basin is longer than the vibrational period. So we expect that the hopping mechanism will break down when the separation of time scales between vibrational and hopping motions is violated. This appears to be the case for the high temperature liquids shown in Fig. 3.

Also evident in Fig. 3 is that most of the cage correlation function has decayed due to the fast vibrational motion. After 1 ps, $C_{\text{cage}}(t)$ has already decayed by an order of magnitude. Therefore, to obtain good statistics for the hopping rate, one must obtain data for many changes in the neighbor lists. For this reason, our data collection is done over 20 ps when the hopping time is only around 1 ps (see Sec. III for details on the specifics of the simulations).

The choice of $c=1$ and the out-only cage correlation function may seem arbitrary. There are practical reasons for choosing this combination, however. We have calculated $C_{\text{cage}}(t)$ for values of c that are larger than 1 and for both the in-out (Eq. (10)) and out-only (Eq. (11)) versions of $C_{\text{cage}}(t)$. Plots of the two versions of the cage correlation function (and with different values of c) for a typical liquid are shown in Fig. 4.

The in-out form of the cage correlation function (Eq. (10)) with $c=2$ gives a nearly identical long-time slope to the out-only version (Eq. (11)) with $c=1$, and both appear to be measuring the rate of the same long-time process. With $c=3$ (in-out) and $c=2$ (out-only) the cage can change many times before we register the change, and the decay seems to be governed by the time it takes to make two or three hops instead of a single hop. The in-out form with

$c=1$ decays almost completely due to vibrational motion, which makes it very difficult to get good long-time statistics, since nearly all of the cages have decayed after only 1 ps. We can choose either the in-out with $c=2$ or the out-only with $c=1$ and we will measure the same rate, but the out-only cage correlation function is computationally cheaper.

Another interesting feature of the cage correlation function is the dependence of the decay on r_{nlist} . We have observed that there is a value for r_{nlist} which minimizes the number of changes in the atomic cages. This has a simple explanation—if r_{nlist} is too small, vibrations from the first solvation shell will contribute to the decay of the cage correlation at short times and will increase the total number of cage changes. If r_{nlist} is too large, vibrations from the second solvation shell will also result in rapid changes to the atomic surroundings. Therefore, minimizing the number of cage changes can be used to set r_{nlist} variationally, and we have used this procedure in all subsequent calculations.

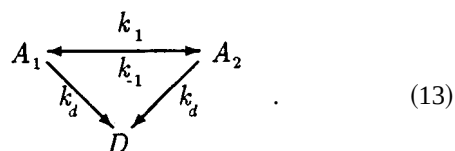
We expect that the short time behavior of $C_{cage}(t)$, which determines the mechanism for hopping to a nearby local minimum, will be sensitive to our choice of the definition of the cage (the value of r_{nlist}). However, we have observed that the slope of the *long time* decay of $C_{cage}(t)$ is not sensitive to reasonable changes in r_{nlist} .

B. The kinetic scheme

Our model of self-diffusion is conceptually quite simple, and is quite obvious in light of the time dependence of C_{cage} . The model assumes that atoms are locked within a cage (A) until they can make a hop to another cage (D). As an atom moves around in its cage, it can see surroundings that differ slightly from the original surroundings. It is still locked in the cage, however, and these fast changes in the surroundings do not represent diffusive hoppings between basins.

The different configurations of the cage atoms are denoted ($A_1, A_2, \dots$), and the cage atoms can shift between these different configurations rapidly. The rapid transfer between cage configurations is characterized by fast rate constants for the forward (k_1) and backwards (k_{-1}) directions. Atomic transfer to another cage is relatively rare, however, and once an atom has entered the new cage (D), it does not return. The relatively rare transfer of atoms between cages is characterized by a slow rate constant, k_d .

The kinetic mechanism for diffusion in this model is



The solution to the kinetic mechanism is obtained easily with the standard Laplace transform or matrix methods,³⁹ and assuming that all of the atoms in the system start in A_1 , the number of atoms remaining in A_1 at time t is

$$[A_1](t) = \frac{[A_1]_0}{k_1 + k_{-1}} (k_1 e^{-(k_1 + k_{-1} + k_d)t} + k_{-1} e^{-k_d t}). \quad (14)$$

Assuming that $k_{-1} = k_1$, this simplifies to

$$[A_1](t) = \frac{[A_1]_0}{2} (e^{-(2k_1 + k_d)t} + e^{-k_d t}). \quad (15)$$

This kinetic mechanism exhibits exactly the same double-exponential behavior that we observe in the cage correlation function. If we understand the species A_1 to be the atom in its original cage, then it is clear that the slow rate in this mechanism (k_d in both Eq. (14) and Eq. (15)) is identical to the hopping rate out of the cage. Now that we have identified the hopping rate, our method for calculating diffusion constants is quite simple:

- (1) Run short trajectories and store atomic positions.
- (2) Compute $C_{cage}(t)$ from stored atomic positions.
- (3) Fit long-time decay of $C_{cage}(t)$ to obtain hopping rate.
- (4) Obtain $\rho_q(\omega)$ from quenches of some of the stored configurations.
- (5) Use the Zwanzig formula (Eq. (2)) to calculate the diffusion constant.

The only part of this method that requires computational effort above and beyond standard trajectory methods is the calculation of $\rho_q(\omega)$, which involves following the steepest descent path to the nearest local minimum on the surface followed by a diagonalization of the force constant matrix. To obtain good statistics for $\rho_q(\omega)$, this procedure must be done for a few statistically independent liquid configurations. Note that $\rho_q(\omega)$ is nearly independent of temperature, so one must compute it only once for each density.

An alternative method for estimating $\rho_q(\omega)$ is the quench echo technique of Nagel *et al.*,⁴⁰ but for small simulations it is computationally less expensive to diagonalize the force constant matrix. Also, since $\rho_q(\omega)$ contains information about the vibrational frequencies in the basins, it should (in principle) be possible to obtain the same information from the fast decay of $C_{cage}(t)$ although we have not yet found a method to do this, and on rough potential energy surfaces, $\rho_q(\omega)$ may not be related in a simple fashion to vibrational motion of atoms in their respective cages.

C. Limitations of the model

If the potential energy surface is rough, i.e. if it has an oscillating or random perturbation superimposed on a smooth background, one would expect an additional contribution to the fast decay. In liquids the fast decay channel can be associated either with the vibrational motion or with the rapid recrossing of the small barriers on the rough surface. (These barriers can be considered small only when the temperature is very much in excess of their average height.) In the high temperature liquids, we are lumping the small barrier crossing motions together with the vibrations since they are comparable in time scale and contribute to the decay of the neighbor list correlation function in a similar fashion. Both the pure vibrational motion and the rapid recrossing of smaller barriers will contribute to the changes in the neighbor list at short times and both can be counted on to return the neighbor list to its initial state.

At temperatures comparable to the average height of the smaller barriers (which is a measure of the roughness),⁴¹ crossing the smaller barriers requires activation, and one would expect that there would be a sharp drop-off in the diffusion constant.⁴² Therefore, near the glass transition temperature (T_g), lumping the small barrier crossings together with the vibrations is incorrect. The atoms now have to diffuse across the smaller basins in order to get to the barriers between larger basins. Our kinetic model does not take these smaller barriers into account, and we must point out that near T_g , one should be very careful in interpreting the vibrational and hopping decay rates obtained from the neighbor list correlations.

III. RESULTS

We performed molecular dynamics simulations on systems of particles interacting via the Lennard-Jones potential

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - V_{\text{cut}}, \quad (16)$$

with parameters chosen to approximate the interactions between argon atoms ($\epsilon = 0.2381$ kcal/mol, $\sigma = 3.405$ Å).^{28,43} V_{cut} is the standard Lennard-Jones potential evaluated at the cutoff radius ($r_{\text{cut}} = 10$ Å) outside of which the potential energy is set to 0. The lower-density ($\rho^* = 0.75, 0.85, 0.94$) simulations were carried out with 108 particles, and at the higher density ($\rho^* = 1.0$) we carried out simulations with 256 atoms.

All of the liquid, supercooled liquid, and glass simulations were started with the atoms in the face-centered-cubic (fcc) lattice, and with velocities sampled from a Maxwell-Boltzmann distribution with a temperature that was at least four times the melting temperature. Following a 60 ps period of equilibration, we quenched the atomic positions to the nearest local minimum on the potential energy surface using the standard steepest-descent method. Following the quench, the velocities were resampled from a Maxwell-Boltzmann distribution with a temperature twice the target temperature for the simulation. Another short equilibration of 20 ps followed the resampling of the velocities, and a 20 ps data collection run began at the end of the equilibration. Diffusion constants were calculated via the Einstein relation during a longer (200 ps) run following the same equilibration steps. This equilibration procedure ensured that the initial configurations for the trajectories were disordered liquids or glasses, even when the desired temperatures are well below the melting temperature. We monitored the temperature and the pair correlation function, $g(r)$, throughout the runs to verify that the liquids, supercooled liquids, and glasses did not crystallize during equilibration or data collection.

Simulations of the solids were done in a similar manner, although the initial 60 ps equilibration steps at temperatures above the melting temperature were omitted for these runs.

During the trajectory calculations, we saved the atomic positions every ten time steps. These configuration were later used to compute the neighbor list (Eq. (7)) and cage correlation (Eq. (11)) functions.

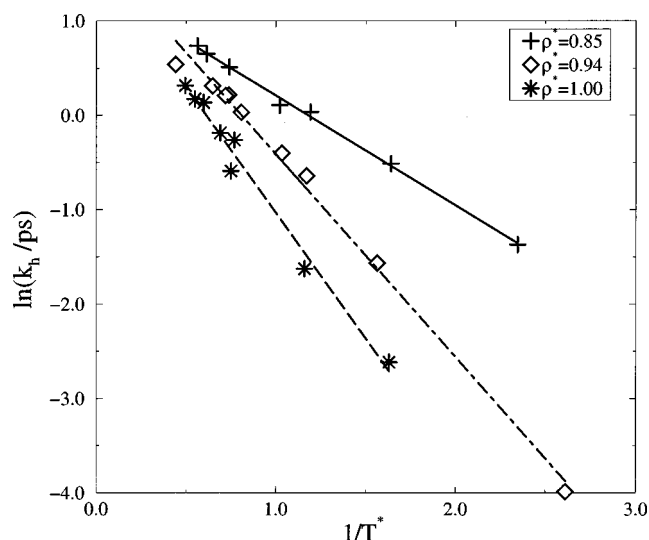


FIG. 5. An Arrhenius plot of the hopping rates between basins for three densities. Error bars have been omitted from the plot because they are smaller than the symbols used. Linear fits to the measured hopping rates are also shown. The slopes of the linear fits are used in estimating the activation energy in Table I.

A. The hopping rate

Using the model presented in Sec. II, we can compute the hopping rate, which we identify with the slope of the long-time decay of the $C_{\text{cage}}(t)$. An Arrhenius plot of the hopping rates ($k_h = A \exp(-E_a/kT)$) is shown in Fig. 5 for three different densities and for a wide range of temperatures. As expected, the rate increases with decreasing density at a given temperature.

All three densities exhibit an Arrhenius-type behavior in liquids and supercooled liquids over the entire temperature range. This is not the case for the lower density ($\rho^* = 0.75$), which we have not shown in Fig. 5. The hopping rate at this density depends linearly on the temperature, which is what one would expect if the decay was due solely to vibrational motion. This indicates to us that the hopping mechanism has broken down at the lowest density, i.e. there is no longer a separation of time scales between vibrational motion and barrier hopping.

The value of the activation energy in reduced units ($E_a^* = E_a/\epsilon$) is summarized in the table provided in Sec. IV. The average barrier height, which we associate with the activation energy, increases with increasing density. The close packing of the atoms at high densities forces a diffusing atom to hop over larger barriers.

B. Self-diffusion constants

Using the estimated hopping rates calculated from the decay of $C_{\text{cage}}(t)$ we can apply Zwanzig's model (Eq. (2)) and calculate the self-diffusion constant. The quenched density of states $\rho_q(\omega)$ in Eq. (2), is obtained by computing the normal-mode frequencies for a collection of quenched liquid configurations. These are obtained by following the steepest-descent path to the nearest local minima for a sequence of

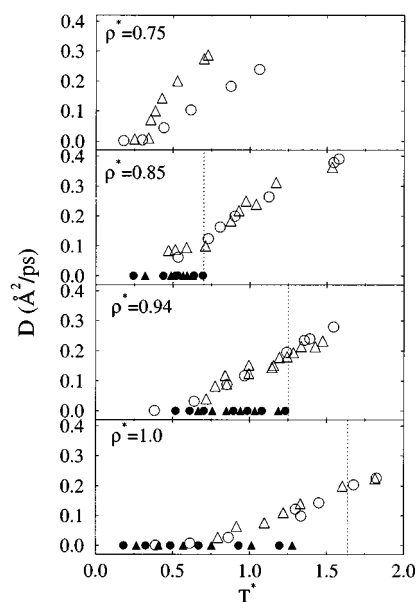


FIG. 6. Plots of the temperature dependence of the diffusion constant for four different densities. The circles ($\circ$) are diffusion constants calculated via the Cage correlation function (Eq. (11)) combined with the Zwanzig formula (Eq. (2)) and the triangles ($\triangle$) are the diffusion constants calculated via the Einstein relation (Eq. (3)). Open symbols are results for supercooled and regular liquids and filled symbols are results for solids. The dashed lines indicate the solid-liquid phase transitions at $T^* = 0.69, 1.20$, and 1.65 , for $\rho^* = 0.85, 0.94$, and 1.0 respectively. Vertical error bars have been omitted from the plot because they are smaller than the symbols used.

statistically independent liquid configurations. We have verified that over the relevant temperature range, $\rho_q(\omega)$ is independent of temperature.

Self-diffusion constants calculated via the cage correlation function combined with the Zwanzig formula (Eq. (2)) have been plotted along with diffusion constants calculated via the Einstein relation (Eq. (3)) in Fig. 6. In contrast to the instantaneous normal mode theories,²⁶ the diffusion constants calculated via the cage correlation function are effectively zero for crystalline solids. Note that the data presented in Fig. 6 are obtained from constant energy trajectories, so the largest uncertainties are along the temperature axis. The data points each have a standard error of 0.06 in reduced temperature units along this axis.

The present theory does quite well at predicting the diffusion constant in the high density fluids for a wide range of temperatures. At the lowest density shown ($\rho^* = 0.75$), the agreement is poor. This indicates that the hopping mechanism for self-diffusion in liquids breaks down at the lower density, and can be considered relevant only for moderate to high density liquids.^{44,45}

IV. DISCUSSION

The primary aim of Sec. II was to provide a simple method to compute the hopping rate between basins. In Sec. III we illustrated how well the model works over a wide temperature and density range for Lennard-Jones systems. Now we will look deeper into the underlying physical pro-

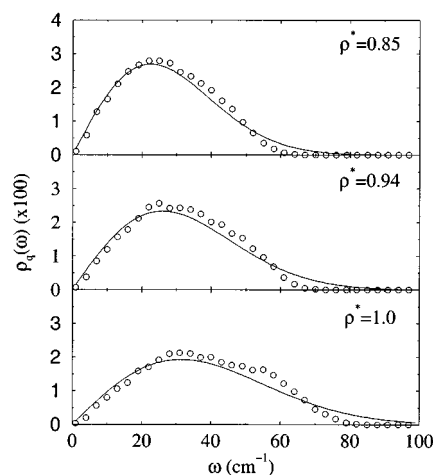


FIG. 7. Fits to the normalized quenched density of states ($\rho_q(\omega)$) using the functional form in Eq. (17) for liquids of 3 different densities.

cesses of diffusion. We begin by deriving an approximate expression for the self-diffusion constant. The underlying assumptions are the following:

- An Arrhenius behavior of the hopping rate. In Sec. III we have shown that this is the case for the medium and high density Lennard-Jones fluids. At very high temperatures (for supercritical fluids) and at low liquid densities, this assumption breaks down. As discussed in Sec. III we believe that this is a sign that the hopping mechanism itself is incorrect for very high temperatures and low densities. Deviations from Arrhenius behavior can also occur at very low temperatures (near T_g) where the roughness of the surface requires careful treatment.
- The liquid's quenched density of states is approximated by the following functional form

$$\rho_q(\omega) = 2\alpha\omega \exp(-\alpha\omega^2), \quad (17)$$

which scales linearly at low frequencies and has a high frequency Gaussian cutoff.⁴⁶ α is a free parameter estimated from a nonlinear fit to the quenched density of states. This form fits the computed results reasonably well. It deviates at high frequencies, where the quenched density of states decays faster than the Gaussian cutoff. Typical fits to the quenched density of states are shown in Fig. 7.

Inserting Eq. (17) into the Zwanzig self-diffusion expression (Eq. (2)) and integrating over the frequency yields

$$D = \frac{kT}{M} \alpha k_h \exp(\alpha k_h^2) (-\text{Ei}(-\alpha k_h^2)), \quad (18)$$

where $\text{Ei}(x)$ is an exponential integral function⁴⁷ and $k_h = A \exp(-E_a/kT)$ is the hopping rate. The values of the activation energy, the pre-exponential factor and the inverse width of the quenched density of states were obtained from the decay of the cage correlation function, and are summarized in Table I.

TABLE I. The activation energy ($E_a^* = E_a / \epsilon$), the pre-exponential factor ($A^* = A / (\epsilon / (m \sigma^2)^{1/2})$) obtained from an Arrhenius fit to the computed hopping rates, and the inverse width ($\alpha^* = \alpha \epsilon^2$) obtained from a non-linear fit to the quenched density of states for three different densities. All quantities are expressed in reduced units for the Lennard-Jones potential.

ρ^*	E_a^*	A^*	α^*
0.85	1.16	8.6	6.84
0.94	1.93	10.3	5.11
1.00	2.66	11.0	3.51

Since αk_h^2 is typically much smaller than unity, we can use an asymptotic form for the exponential integral⁴⁸ to obtain

$$D = \frac{kT}{M} \frac{\chi}{k_h} \exp(\chi) (-\gamma - \ln(\chi)), \quad (19)$$

where $\chi = \alpha k_h^2$ and $\gamma = 0.5772156649 \dots$ is Euler's constant.⁴⁸ Self-diffusion constants calculated via Eq. (19) are shown in Fig. 8 along with the results obtained using the cage correlation function and the Einstein relation (Eq. (3)).

The simple analytical formula (Eq. (19)) provides a realistic approximation to the self-diffusion constant. It captures both the magnitude of the self-diffusion constant and its temperature dependence. However, its main advantage is that it highlights the parameter that governs the magnitude of the self-diffusion constant—the ratio between the hopping rate, k_h and the frequency width of the quenched density of states, $1/\alpha$, which is given by $\chi = \alpha k_h^2$.

In the literature concerning diffusion in amorphous materials, liquids are often classified as *strong* or *fragile* based on the temperature dependence of the diffusion constant near

T_g . In the strong limit, the diffusion displays Arrhenius temperature dependence,^{41,49} while in fragile liquids, there is a crossover from Arrhenius to a super-exponential ($\exp(-(T_0/T)^2)$) temperature dependence as the temperature is lowered to T_g .^{41,49}

It is believed that this difference in the temperature dependence of the diffusion constant arises from the size of diffusive barriers relative to the average barrier height that characterizes the roughness of the potential energy surface.^{49,50} In the strong limit, the potential energy surface is thought to be uniformly rough (the energy gap between the small and large barriers is negligible, or all of the barriers are barriers to diffusion), while atoms in fragile liquids have to become activated to cross the small barriers in addition to the larger diffusive barriers. At temperatures well in excess of T_g , these barriers are crossed easily, and the diffusive barriers result in simple Arrhenius-like temperature dependence. As the temperature falls, atoms must diffuse across the small barriers to reach the diffusive barriers, so the diffusion constant can display the super-exponential temperature dependence.⁴¹

Keyes (using an instantaneous normal mode approach) has observed this crossover in Lennard-Jones systems to occur just above T_g ,⁵¹ but in normal glasses the superexponential behavior can persist over a wider range of temperatures.^{52,53}

If one were to look at the temperature dependence of our analytical expression for the diffusion constant in Eq. (19), one would see an almost perfect Arrhenius-like behavior. We should note, however, that our simple approximation to the self-diffusion constant fails to predict the low-temperature crossover to the super-exponential behavior which has been observed in real glasses.⁵² Therefore, at temperatures near T_g the diffusion process will depend strongly on the heights of the small surface-roughening barriers and we expect an additional key mechanism to interfere with the diffusive barrier hopping, which will strongly decrease the hopping rates from our calculated values. We therefore caution readers about applying our simple approach in cases where there are more than two time scales in the decay of $C_{\text{cage}}(t)$, as a second slow decay mechanism may indicate the crossing of the smaller barriers.

V. CONCLUSIONS

In the preceding pages, we have presented a method for using molecular dynamics simulations to estimate the hopping rate for the Zwanzig model of self-diffusion (Eq. (2)). We associate the hopping rate with the slow decay of the cage correlation function (Eqs. (10) and (11)), while we assign the fast initial decay either to simple vibrational motion or to barrier crossing rates of the small perturbing barriers on a rough potential energy surface—barriers which are not the barriers to diffusion.

There is excellent agreement between the self-diffusion constants calculated with our method and those calculated via the Einstein relation (Eq. (3)) over a wide range of temperatures and densities. This agreement holds both in the

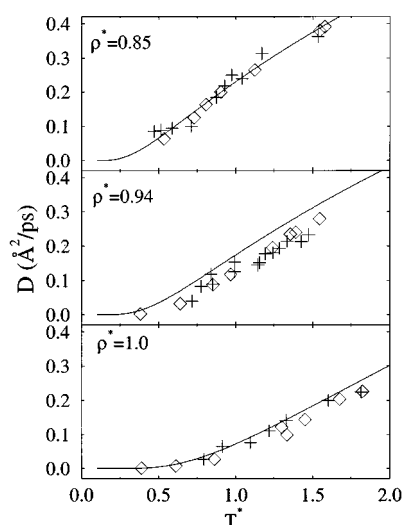


FIG. 8. Plots of the diffusion constant for three different densities. The diamonds ($\diamond$) are diffusion constants calculated via the cage correlation function (Eq. (11)) combined with the Zwanzig formula (Eq. (2)) and the crosses (+) are the diffusion constants calculated via the Einstein relation (Eq. (3)). The curves are the results obtained using Eq. (19). Note the sudden change in the self-diffusion constant near the liquid-glass transition ($T_g^* \approx 0.34$ for $\rho^* = 1.0$) (Ref. 24). Vertical error bars have been omitted from the plot because they are smaller than the symbols used.

supercooled and regular liquids, and we are also able to predict the large drop in the diffusion constant for solids. (We also note that this method can calculate diffusion constants using simulations that are substantially shorter than those required to obtain good results using the Einstein relation.)

Additionally, we have shown that at low densities (and possibly at higher temperatures), the time scales for vibrational motion and basin hopping merge, and the Zwanzig model for diffusion begins to break down. It might be useful at the higher temperatures to use the procedure introduced by Cao and Voth which accounts for some of the anharmonicities within each basin.^{14,15} At lower densities, we must look for a different mechanism for self-diffusion, since the atoms reside in each basin for less than a vibrational period.

We have also used an approximation to the vibrational density of states in the liquid ($\rho_q(\omega)$) to derive a simple analytical model for the self-diffusion constant in liquids and supercooled liquids. This simple model also gives quantitative agreement with the correct diffusion constants.

There remain a few loose ends in this work that we will attempt to tie up in the future. We believe that there may be a way to estimate the vibrational density of states in the liquid using the *fast* decay of the cage correlation function, but we have not been able to make this connection in this paper. There are also some subtleties about the decay of the cage correlation function at temperatures that are near the glass transition temperature (T_g), and resolving the hopping rate on rough surfaces may need a more thoughtful treatment than we have provided above.

The cage and neighbor list correlation functions are quite intriguing quantities, and in future work we will be investigating their usefulness in other areas of molecular simulations.

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