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Liquid dynamics theory of the velocity autocorrelation function and self-diffusion

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In equilibrium liquid dynamics theory, the potential energy surface is supposed to consist of a large number of many-particle nearly harmonic random structural valleys. The passage of the system from one valley to another is a *transit*, and the transit motion has to be accounted for in order to apply liquid dynamics theory to nonequilibrium processes. The role of transits in liquid dynamics theory is equivalent to the role of collisions in gas dynamics theory. In a classical monatomic liquid, transits are so frequent that each ion ''sees'' a rapidly fluctuating well during one mean vibrational period. This condition is represented approximately by an independent ion model, in which each ion moves in a smooth harmonic well of frequency ω, and at each classical turning point the ion enters a new well with probability μ, or returns in its old well with probability $1-\mu$. The corresponding velocity autocorrelation function, which depends on ω and a simple function $\xi(\mu)$, can be made to fit previously published computer calculations. The frequency ω is close to the mean phonon frequency of the crystalline state, confirming a prediction of equilibrium liquid dynamics theory, and the transit probability μ is around $\frac{1}{2}$. Analysis of experimental diffusion data suggests that ξ is approximately a universal function of T/T_m. [S1063-651X(98)08007-6]

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I. INTRODUCTION

The equilibrium theory of liquid dynamics was developed recently [1]. The key ideas are the following: (a) The ions move primarily within one or more macroscopically similar nearly harmonic random structural valleys in the potential energy surface. (b) The number of such valleys is approximately the universal number w^N for an N-ion system. Property (a) gives the ion-motional specific heat of approximately $3Nk$ for classical monatomic liquids, in agreement with experiment [1]. Property (b) gives a universal contribution $Nk \ln w$ to the entropy of melting at constant volume, also in agreement with experiment [2]. These contributions to specific heat and entropy are the leading (quasiharmonic) contributions. Liquid dynamics theory also predicts corrections arising from anharmonic distortions of the potential energy valleys, and from the presence of intersections of neighboring valleys. The high-temperature specific heat of classical monatomic liquids has been rationalized in terms of these two corrections [3].

In passing, we are using notation from electronic structure theory, where each nucleus plus rigid electron core is called an ion, and where the outer (valence) electrons are viewed as continuously deforming when the ions move. The reader may feel free to substitute the word nucleus, or atom, for ion, throughout this paper.

It is useful now to attempt an application of liquid dynamics theory to nonequilibrium processes. In contrast to equilibrium theory, where it is only necessary to recognize the intersections of neighboring valleys as a boundary condition in the partition-function integration, in nonequilibrium theory it is necessary to account for the actual motion of the ion system, when it crosses these intersections. The motion of the ion system at the instant of passing from one valley to another is called a transit. The role of transits in liquid dynamics theory is equivalent to the role of collisions in gas dynamics theory.

In the present paper, we study the simplest nonequilibrium process in a classical monatomic liquid, self-diffusion. The statistical description of self-diffusion is conveniently expressed in terms of the velocity autocorrelation function $Z(t)$, and its integral, which is the self-diffusion coefficient D [4]. In Sec. II, from an examination of the ion motion in classical monatomic liquids, we are led to propose an independent ion model as the leading-order description of this motion. The velocity autocorrelation function for the independent ion model is worked out in Sec. III. This function is compared with previously published computer calculations in Sec. IV. The theoretical self-diffusion coefficient provides a basis in Sec. V for rationalizing experimental measurements on normal melting elemental liquids. Our conclusions are summarized and discussed in Sec. VI.

Before proceeding, we should relate the present work to a major current program in describing the motion of particles in the liquid and supercooled liquid states. The description is based on the instantaneous normal modes (INM's), which were introduced for an amorphous system by Rahman, Mandell, and McTague [5], and for crystal and liquid systems by LaViolette and Stillinger [6]. The INM's are the eigenvalues and eigenvectors of the potential energy curvature tensor, evaluated at the instantaneous configuration of the many-particle system. The INM spectrum contains a temperature-dependent lobe of negative eigenvalues, called the ''unstable'' modes. Buchner, Ladanyi, and Stratt [7] expanded the short-time dynamics of a many-particle system in terms of the instantaneous positions, velocities, forces, and the INM's, and derived the corresponding short-time expansion of various autocorrelation functions. By intercomparison of computer calculations, these authors concluded that the short-time expansion is improved by omitting the contributions from unstable modes. This procedure was subsequently applied to calculate the velocity autocorrelation function for liquid and glassy cesium by Vallauri and Bermejo [8]. Keyes and co-workers [9,10] developed a different approach to the problem of extending the exact short-time dynamics into the longer-time regime appropriate for diffusive motion. They argued that unstable modes are present because the many-particle system crosses barriers, and they formulated a statistical description of the motion in terms of the distribution of barrier heights. The description was applied to calculate the velocity autocorrelation function of supercooled Ar [10], and work on the barrier height distribution continues [11]. In a still different procedure, Cao and Voth [12] introduced a reference system consisting of effective harmonic oscillators, and used a variational calculation based on the Gibbs-Bogoliubov inequality to find the self-consistent temperature-dependent reference system, which they called the optimized quadratic approximation. To calculate time correlation functions, Cao and Voth [13] replaced the true potential by the optimized quadratic potential at each inherent structure, then modeled the decay of correlations which results when the system moves from structure to structure. The inherent structures are those originally introduced by Stillinger and Weber [14,15].

The present approach begins with the picture of the many-particle potential surface as composed of a large number of nearly harmonic valleys. The motion of the system within a single valley is approximately expressed in terms of the ordinary (stable) normal modes of that valley. This approach was satisfactory for evaluating the liquid partition function [1], but now, when we attempt to follow the system motion, we soon realize that the set of normal modes changes so rapidly, as the system moves from valley to valley, that the single-valley normal modes are not useful in describing the motion. This is essentially the same problem as presented by the ever-changing instantaneous normal modes, in which context the problem is being addressed by the theoretical program outline above. Here we address the problem by abandoning normal modes, and by starting over from the opposite picture of nearly independent ion motion. Our aim is to investigate whether or not this new starting point might be useful in describing the motion of particles in the liquid state.

II. INDEPENDENT ION MODEL

In equilibrium statistical mechanics, in calculating the partition function, one has to integrate the canonical weight factor $\exp(-\beta\Phi)$, where $\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the many-particle potential as function of the entire set of ion positions $\mathbf{r}_K$, $K=1,...,N$. The straightforward approach to this integral is to express Φ approximately as a sum over independent coordinates. Hence, in liquid dynamics, we have expressed Φ as a set of approximately independent many-particle valleys, and within each valley, as a set of approximately independent many-particle normal modes [1]. Then, in this quasiharmonic approximation, the integral of $\exp(-\beta\Phi)$ is trivial. To proceed now to nonequilibrium statistical mechanics, we need to make an approximate description of the motion of each separate ion in the system. Our first thought would be to resolve the motion of a single ion into two contributions, in the following manner: (a) when the system is within a single many-particle potential valley, express the motion of a single ion as a sum over all normal modes; and (b) add the single ion motion which occurs each time the system makes a transit from one many-particle valley to another. However, as we proceed along this line, we will discover that an entirely different resolution is appropriate for the monatomic liquid state.

In nonequilibrium statistical mechanics, one has to construct a statistical description which is local in space and time, that is, which applies to intervals of space and time macroscopically small, but still large enough to support a statistical description. The reason for this is that the irreversible processes which drive a many-particle system toward equilibrium, and which arise directly from the Hamiltonian motion of the system, are local in space and time [16]. Hence in liquid dynamics, as already observed in Ref. [1], the transit motion which carries the entire system from one many-particle valley to another must be local, involving only a small local group of ions. The transit rate is then a local function, expressed as the number of transits per time per volume. Correspondingly, we have developed the following picture of a transit: a small group of ions, say two or three, reaches a point in the ions' motion where simultaneously, or within a very small interval of time, the ions' restoring forces change so as to direct them toward new, significantly displaced, equilibrium positions. The key to this process is correlation among the positions and momenta of the transiting ions and their neighbors: the transit occurs only if the necessary correlation is present.

In passing, let us note the analogy with the theory of a dilute gas. For equilibrium statistical mechanics, with $\Phi=0$ in the leading approximation, the configuration integral is done by moving each particle independently over the entire volume of the gas container, and no consideration of collisions is required [17]. On the other hand, for nonequilibrium statistical mechanics, the Boltzmann theory is constructed at the outset in terms of the highly local collision process, and, for a collision to occur, two particles must have the proper position and velocity correlation [18].

Let us now consider a single ion, with a mean vibrational period of τ, in a monatomic liquid. From analysis of experimental data for self-diffusion in liquids, and data for bulk and shear viscosities as well, we have reached the conclusion that this single ion will participate in a transit on average once in every time interval τ, very approximately. This means the ten or so near neighbors of an ion are involved in transits many times during one vibrational period, and each transit alters the eigenvectors of the normal modes of the local group of ions. Hence the normal modes cannot serve as a useful basis for analyzing the motion of any single ion. The appropriate starting point is apparently to picture each ion as oscillating in a fluctuating well. The obvious next step is to replace the fluctuating well by its average, as an approximation. Consistent with this picture, we suppose that each ion moves in a smooth harmonic well, and, when it reaches a classical turning point, that it will transit to a new well with a certain probability, or otherwise will move back within its present well.

The strong correlations among the moving ions in the liquid state are built into this picture in two ways. First, the correlation among ion positions, which prohibits them from approaching one another closely in the liquid state, and which therefore supports the picture of many-particle potential energy valleys [1], is contained in the presence of a localizing well ‘‘seen’’ by each ion. Second, the correlation required for a transit to occur is contained in the probability factor, which expresses whether an ion at a turning point will see a continuation of the same potential well it has moved in, or will see a new potential well to enter. Having constrained the ion motion in these two ways, we neglect all further correlations, and allow each ion to move independently. This defines the present liquid dynamics independent ion model.

An important part of the above argument is the high rate of occurrence of transits, specifically that each ion transits approximately once in a time interval τ. For simplicity of argument here, we will take this as a hypothesis, to be confirmed shortly by our comparison of theory and experiment for the velocity autocorrelation function.

III. MODEL FOR THE VELOCITY AUTOCORRELATION FUNCTION

Consider an ion with position $\mathbf{r}(t)$ and velocity $\mathbf{v}(t)$, where t is time. The ion moves in a sequence of harmonic wells, all having a common zero of energy, and a common angular frequency ω. At each turning point, where $\mathbf{v}=0$, the ion can transit to a new well, or can remain in the old well. At the transit, the position and velocity are conserved, but the new well has a location different from the old well. Since the ion enters a new well at a turning point, and accelerates toward the well center, we collect the three Cartesian oscillators into one vector oscillator which passes through the well center. In a well centered at $\mathbf{R}$, we write $\mathbf{r}=\mathbf{R}+\mathbf{a}\sin(\omega t+\alpha)$, and $\mathbf{v}=\omega\mathbf{a}\cos(\omega t+\alpha)$, where $\mathbf{a}$ is the amplitude vector, and α is the initial phase. The energy is conserved, so $a=|\mathbf{a}|$ is a constant of the motion.

The ion oscillator starts with phase α at $t=0$, $-\pi/2\leqslant\alpha\leqslant\pi/2$. We divide the motion into sequential intervals called cycles, where each cycle ends at a turning point. The cycle time intervals are as follows.

$$\text{Cycle 1:}\quad 0\leqslant\omega t\leqslant\frac{\pi}{2}-\alpha, \tag{1}$$

$$\text{Cycle } m\text{:}\quad \left(m-\frac{3}{2}\right)\pi-\alpha\leqslant\omega t\leqslant\left(m-\frac{1}{2}\right)\pi-\alpha,$$

$$m=2,3,\ldots.$$

The position vector in cycle m is $\mathbf{r}=\mathbf{R}_m+\mathbf{a}_m\sin(\omega t+\alpha)$, $m=1,2,\ldots.$

The velocity autocorrelation function is

$$Z(t)=\tfrac{1}{3}\langle\mathbf{v}(t)\cdot\mathbf{v}(0)\rangle=\tfrac{1}{3}\omega^2\langle\mathbf{a}(t)\cdot\mathbf{a}(0)\cos(\omega t+\alpha)\cos\alpha\rangle. \tag{2}$$

This is a complete ensemble average. We will first do the average of initial phases, over $-\pi/2$ to $\pi/2$. Then $Z(t)$ is written on intervals of ωt as follows, where each interval contains contributions from two cycles:

$$0\leqslant\omega t\leqslant\pi:$$

$$Z(t)=\frac{1}{6}\omega^2\left\langle\mathbf{a}_1^2\cos\omega t+\frac{1}{\pi}(\mathbf{a}_1^2-\mathbf{a}_2\cdot\mathbf{a}_1)\times(\sin\omega t-\omega t\cos\omega t)\right\rangle. \tag{3}$$

$$(n-1)\pi\leqslant\omega t\leqslant n\pi:$$

$$Z(t)=\frac{1}{6}\omega^2\left\langle[n\mathbf{a}_n\cdot\mathbf{a}_1-(n-1)\mathbf{a}_{n+1}\cdot\mathbf{a}_1]\cos\omega t+\frac{1}{\pi}(\mathbf{a}_n\cdot\mathbf{a}_1-\mathbf{a}_{n+1}\cdot\mathbf{a}_1)(\sin\omega t-\omega t\cos\omega t)\right\rangle.$$

We now analyze the angle averages involved in the scalar products of amplitude vectors. At the first turning point, $\mathbf{a}_1$ goes to $\mathbf{a}_2$. With probability μ, $0\leqslant\mu\leqslant1$, the ion transits to a new well, having $\mathbf{a}_2\cdot\mathbf{a}_1=a^2\cos\theta$, where $-1\leqslant\cos\theta\leqslant1$. We expect the new well center $\mathbf{R}_2$ to lie roughly in the direction $\mathbf{a}_1$ from $\mathbf{R}_1$, so that $\mathbf{a}_2$ is roughly opposite in direction from $\mathbf{a}_1$, and $\cos\theta<0$. Hence we expect $\langle\cos\theta\rangle$ to be around $-\frac{1}{2}$, where the indicated average is over transits. Proceeding, with probability $1-\mu$, the ion stays in its old well, so that $\mathbf{a}_2=\mathbf{a}_1$ and $\mathbf{a}_2\cdot\mathbf{a}_1=a^2$. Then, averaging over transits gives

$$\langle\mathbf{a}_2\cdot\mathbf{a}_1\rangle=\mu a^2\langle\cos\theta\rangle+(1-\mu)a^2=a^2\{1-[1-\langle\cos\theta\rangle]\mu\}. \tag{4}$$

Since we will have no way in this study of separating the parameters μ and $\langle\cos\theta\rangle$, we put them together in a net transit parameter ξ, defined by

$$\langle\mathbf{a}_2\cdot\mathbf{a}_1\rangle=a^2(1-\xi). \tag{5}$$

Formally, $0\leqslant\xi\leqslant2$. However, since we expect $\langle\cos\theta\rangle\approx-\frac{1}{2}$, and we further expect $\mu\approx\frac{1}{2}$, then we anticipate finding $\xi\approx\frac{3}{4}$ for the liquid state.

Now, at the second turning point, a complication arises. The extension of Eq. (4) is

$$\langle\mathbf{a}_3\cdot\mathbf{a}_1\rangle=a^2[\mu^2\langle\cos\theta\cos\phi\rangle+2\mu(1-\mu)\langle\cos\theta\rangle+(1-\mu^2)], \tag{6}$$

where θ and ϕ measure the change in direction of the amplitude vector on two successive transits. The coupled average in Eq. (6) depends on the unknown distribution of $\cos\theta$. However, the most important part of $Z(t)$ is at small t, say, for $\omega t\lesssim2\pi$, and multiple transits have small effect here, so an approximation is acceptable for transits after the first. We take the approximation $\langle\cos\theta\cos\phi\rangle\approx\langle\cos\theta\rangle^2$. Extending this to all multiple transits yields

$$\langle\mathbf{a}_n\cdot\mathbf{a}_1\rangle\approx a^2(1-\xi)^{n-1},\quad n=3,4,\ldots. \tag{7}$$

At this point, the results for $Z(t)$ become

$$0 \leqslant \omega t \leqslant \pi:$$

$$Z(t)=\frac{1}{6}\,\omega^2\left\langle a^2\left[\cos\omega t+\frac{1}{\pi}\,\xi(\sin\omega t-\omega t\cos\omega t)\right]\right\rangle,$$

$$\pi \leqslant \omega t \leqslant 2\pi:$$

$$Z(t)=\frac{1}{6}\,\omega^2\left\langle a^2\left[(1+\xi)(1-\xi)\cos\omega t + \frac{1}{\pi}\,\xi(1-\xi)(\sin\omega t-\omega t\cos\omega t)\right]\right\rangle, \tag{8}$$

and so on.

From the arguments of Sec. II, the remaining correlation in Eq. (8), between the amplitude a and the transit parameter ξ, should be weak. We neglect this correlation, and collapse the average to $\langle a^2\rangle$. Classical statistical mechanics for a three-dimensional harmonic oscillator gives

$$\langle a^2\rangle = 6kT/M\omega^2, \tag{9}$$

where M is the oscillator mass. The reduced velocity autocorrelation function $\hat{Z}(t)$ is defined by

$$Z(t)=Z(0)\hat{Z}(t), \tag{10}$$

and from Eqs. (8) and (9) we find

$$Z(0)=\tfrac{1}{6}\omega^2\langle a^2\rangle = kT/M. \tag{11}$$

Our final result for $\hat{Z}(t)$, for the independent ion model, with the two averaging approximations mentioned above, is as follows:

$$(n-1)\pi \leqslant \omega t \leqslant n\pi,\quad n=1,2,\ldots:$$

$$\hat{Z}(t)=[1+(n-1)\xi](1-\xi)^{n-1}\cos\omega t + \frac{1}{\pi}\,\xi(1-\xi)^{n-1}(\sin\omega t-\omega t\cos\omega t). \tag{12}$$

IV. COMPARISONS FOR THE VELOCITY AUTOCORRELATION FUNCTION

Figure 1 shows graphs of $\hat{Z}(\omega t)$ vs ωt [Eq. (12)] for a selection of ξ values. For $\xi=0$, there are no transits, and $\hat{Z}(\omega t)=\cos\omega t$, corresponding to a collection of independent harmonic oscillators. For $0<\xi<1$, transits occur but are not highly probable, hence most ions move back in the same well at the first turning point, and $\hat{Z}(\omega t)$ dips negative. For $\xi>1$, the transits dominate, most ions move forward into a new well at the first turning point, and $\hat{Z}(\omega t)$ remains positive. Two conclusions from Fig. 1 are noteworthy. The first is that a wide range of nontrivial behavior emerges from our simple model, already as a function of the single parameter ξ. The second is that transits are an essential process in order to achieve a physically realistic curve of $\hat{Z}(\omega t)$. We will now compare our model with the available results from molecular-dynamic computer calculations.

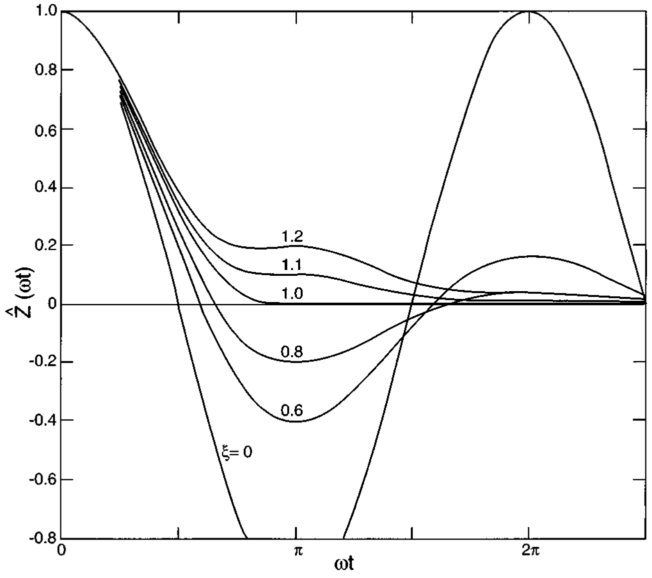

FIG. 1. Reduced velocity autocorrelation function $\hat{Z}(\omega t)$, for various values of the transit parameter ξ, for the independent ion model.

It is fortunate that Mountain and Haan [19] have given us tables of $\hat{Z}(t)$ for liquid Rb, calculated from a realistic potential for metallic Rb, and at densities and temperatures where Rb is in the liquid phase. The densities and temperatures for the three Rb states calculated by Mountain and Haan are listed in Table I. We fitted our $\hat{Z}(t)$, [Eq. (12)] to these calculations, by adjusting the two parameters ω and ξ to obtain agreement at the first minimum in $\hat{Z}(t)$. The fitted ω and ξ are listed in Table I, and the comparison of $\hat{Z}(t)$ curves is shown in Fig. 2. The agreement between our model and the accurate calculations of Mountain and Haan is excellent from $t=0$ to the first minimum in $\hat{Z}(t)$: while $\hat{Z}(t)$

TABLE I. Velocity autocorrelation function data. The first four columns represent computer calculations, from references given in the text. Columns 5–7 represent the present model fitted to the first minimum in $\hat{Z}(t)$. The last column compares the fitted ω with the measured crystal frequency ω_2.

Simulation	T (K)	ρ (g/cm^3)	D (10^{-5} cm^2/s)	ω (10^{13}/s)	ξ	$D(\omega,\xi)$ (10^{-5} cm^2/s)	ω/ω_2
Rb1	345.1	1.501	2.4	0.69	0.69	3.26	1.17
Rb2	436.2	1.501	4.4	0.70	0.75	4.63	1.19
Rb3	606.4	1.348	-	0.64	0.86	8.85	1.23
Na	397	0.927	5.6	1.81	0.75	6.06	1.19
Ar	91	1.428	1.7	0.84	0.89	2.32	(1.7)

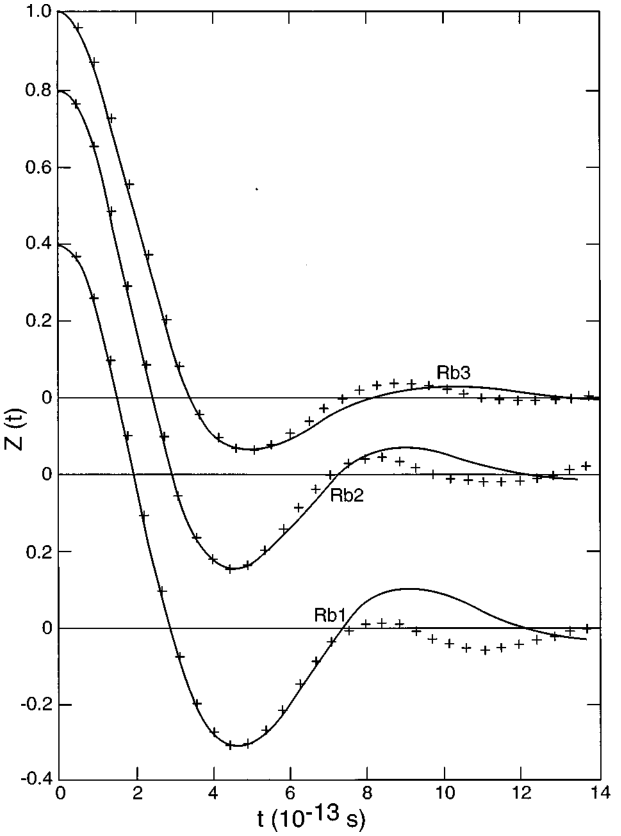

FIG. 2. Comparison of $\hat{Z}(\omega t)$ for the independent ion model (lines) with the molecular-dynamic calculations of Mountain and Haan (symbols).

varies over a range greater than 1, the error of our fitted model is $\lesssim 0.02$. The agreement is still quite good to the zero beyond the first minimum in $\hat{Z}(t)$. Obviously, the simple combination of harmonic oscillations, plus transits, contained in our model accurately captures this most important part of $\hat{Z}(t)$. Beyond the zero after the first minimum, our model retains the correct magnitude, but loses the phase of $\hat{Z}(t)$.

The processes controlling $\hat{Z}(t)$ at large t are complicated. We hope the present model can at least serve as a starting point for trying to evaluate these processes more realistically. Meanwhile, we have one more piece of information on our model $\hat{Z}(t)$ at large t, namely, we have the time integral of $\hat{Z}(t)$. As specified in Sec. V, Eqs. (13) and (14), this integral is related to the self diffusion coefficient D, and the values for our model $\hat{Z}(t)$ are listed as $D(\omega,\xi)$ in Table I. These data compare favorably with the values of D calculated by Mountain [20] for Rb states 1 and 2, and also listed in Table I.

The velocity autocorrelation function, and its integral, was calculated by Rahman [21] for liquid Na, again from a physically realistic potential. Though Rahman provided only a small graph of $\hat{Z}(t)$, an acceptable determination of ω and ξ can still be made, by fitting Eq. (12) to the first minimum, and these parameters for Na are listed in Table I. The comparison of our model $\hat{Z}(t)$, and the corresponding $D(\omega,\xi)$, to Rahman's calculations, essentially duplicates the features of the above comparison for Rb.

For our final comparison, we refer back to Fig. 1, and note that the curves for ξ just below 1, and for ξ just above 1, bear resemblance to the velocity autocorrelation functions calculated for Ar, at two different temperatures, by Levesque and Verlet [22]. But those calculations were done for Ar at a rather low density, where Ar is known to be somewhat gaslike [23,24,1], and for this reason, the present liquid model cannot be made to fit very well the results of Levesque and Verlet. Nevertheless, for the low-temperature Ar state of Levesque and Verlet, we fitted Eq. (25) to the calculated $\hat{Z}(t)$ at the first minimum, and obtained the values of ω and ξ listed in Table I. The corresponding theoretical $D(\omega,\xi)$ compares favorably with D from accurate molecular-dynamic calculations, at the same density and temperature [25], also listed in Table I.

V. ANALYSIS OF EXPERIMENTAL SELF-DIFFUSION DATA

Self-diffusion has been measured in several liquid metals, at temperatures running to a few hundred K above the melting temperature T_m. The level of accuracy is such that equivalent data sets for the self-diffusion coefficient D usually agree within about 10%. Here we analyze representative experimental results for all the normal melting elements for which we were able to find published measurements. In Table II, experimental quantities at T_m are listed, as well as the references for the experimental D vs T data.

Phenomenological accounts of self-diffusion were given by Nachtrieb [33], Brown and March [34], Lodding [35], and Ozelton and Swalin [36], who also gave a brief review of early models. The notion that diffusive jumps of liquid atoms might take place on the vibrational time scale was present already in the work of Nachtrieb [33]. Here we want to interpret the experimental self-diffusion in terms of the independent ion model for liquid dynamics, whose velocity autocorrelation function was worked out and tested in Secs. III and IV. The integral formula for D is [4]

$$D=\int_0^\infty Z(t)dt. \tag{13}$$

By doing the integral of $\hat{Z}(t)$ for each π interval of ωt, from Eq. (12), and summing the results, and multiplying by Eq. (11) for $Z(0)$, the independent ion model yields the simple form

$$D(\omega,\xi)=\frac{4kT}{\pi M\omega}\left(\frac{\xi}{2-\xi}\right), \tag{14}$$

where M is the atomic mass. This is the equation for $D(\omega,\xi)$, whose values are listed in Table I.

At this point, we have a two-parameter model, Eq. (14), for density- and temperature-dependent self-diffusion data. Apart from the examples of Sec. IV, information on the velocity autocorrelation function is not available for calibrating ω and ξ. A universal estimate of the mean vibrational frequency for monatomic liquids would be most helpful here. Fortunately, liquid dynamics theory has given the prediction that, for normal melting elements, the mean vibrational fre-

TABLE II. Experimental data for liquids, where the subscript m denotes ‘‘at melt.’’ References provide the experimental D vs T used in our analysis at $T \geqslant T_m$. Determination of ω_2 and ξ_m is described in the text.

Element	T_m (K)	ρ_m (g/cm^3)	D_m (10^{-5} cm^2/s)	Ref.	$\omega_2(\rho_m)$ (10^{13}/s)	ξ_m
Li	453.7	0.515	5.96	[26]	3.85	0.50
Na	371.0	0.925	4.23	[26]	1.52	0.55
K	336.4	0.829	3.70	[26]	0.93	0.55
Rb	312.6	1.479	2.72	[26]	0.58	0.58
Cu	1357	8.000	3.98	[27]	2.48	0.61
Ag	1234	9.346	2.55	[28]	1.59	0.50
Pb	600.6	10.68	1.74	[29]	0.76	0.60
Zn	692.7	6.58	2.03	[30]	1.94	0.52
In	429.8	7.02	1.68	[31]	1.21	0.68
Hg	234.3	13.69	0.97	[32]	1.10	0.92

quency should be about the same in both liquid and crystal, at the same density [1]. A representative mean vibrational frequency for a crystal is the rms frequency ω_2 [37], defined by

$$\omega_2 = +\sqrt{\langle \omega^2 \rangle_{\mathrm{BZ}}}, \tag{15}$$

where $\langle \omega^2 \rangle_{\mathrm{BZ}}$ is the Brillouin-zone average of the quasiharmonic phonon frequencies squared. Hence ω_2 is related to the phonon characteristic temperature θ_2 [2,24], according to

$$\hbar \omega_2 = \sqrt{3/5}\, k \theta_2 . \tag{16}$$

Extensive tables of highly accurate values of θ_2, based ultimately on inelastic neutron-scattering measurements, have been listed for the crystalline elements [2,24]. Notice that θ_2, and likewise ω_2, depend on density, and can be corrected for small changes in density, by means of the experimental Grüneisen parameter, together with standard formulas [2].

We can test whether or not the crystal ω_2 provides a reasonable estimate of the liquid ω. From the tabulated values of θ_2 for bcc Rb and Na, at densities where the neutron-scattering phonon measurements were performed [2,24], we calculated ω_2, at the densities of the liquid computer calculations given in Table I. The corresponding ratios ω/ω_2 are listed in Table I, where ω was determined in Sec. IV from the calculated velocity autocorrelation functions. For the Rb and Na examples of Table I, while ω varies by a factor of 3, the ratio ω/ω_2 remains around 1.2. This is a striking confirmation that the mean vibrational frequency is about the same in liquid and crystal, at the same density, at least for the alkali metals.

The same ratio ω/ω_2 for Ar is listed in Table I, and should be considered only an estimate because of the very large density correction of ω_2, from the crystal to the liquid density. Even for this somewhat gaslike state of Ar, the characteristic time of the ionic vibration, as indicated by the velocity autocorrelation function, is within a factor of 2 of the characteristic vibration time in the crystal, at the same density.

We now feel safe in using the crystal ω_2 as an estimate for the liquid ω. Values of ω_2 at the density of the liquid at melt are listed in Table II. Now consider Eq. (14). If we use the experimental D for $D(\omega,\xi)$, and if we use the experimental ω_2 for ω, we can solve Eq. (14) for the corresponding value of ξ. The results for liquids at melt are listed in Table II, where one finds ξ_m lying in the fairly narrow range 0.50–0.68 for nine liquid metals, with an outlying value of 0.92 for mercury.

The same analysis was used to find ξ vs T, with experimental D vs T data from the references listed in Table II. Here we used the measured liquid density $\rho(T)$, from sources given previously [1,3], and we evaluated ω_2 at the liquid density as function of temperature. Our results for ξ as function of T/T_m are shown in Fig. 3. Total errors in ξ, including sizable uncertainties in the density correction of ω_2 at high temperatures, and experimental errors in D, are expected to be around ± 0.1. Within such errors, ξ is essentially a universal function of T/T_m, except for mercury, which lies significantly above the other metals in Fig. 3. The increase of ξ with T/T_m, shown in Fig. 3, is consistent with the definition of ξ through Eqs. (4) and (5), since one might expect the transit probability μ to increase weakly both as ρ decreases, and as T increases.

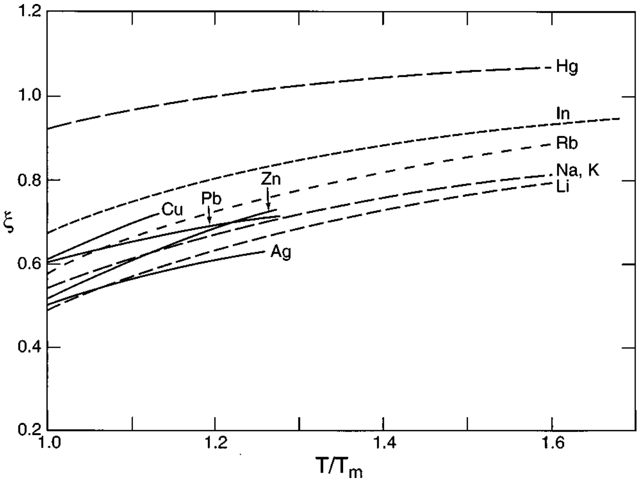

FIG. 3. The transit parameter ξ, determined by fitting the independent ion model, using the crystal frequency $\omega_2(\rho)$, to the experimental D vs T data.

VI. CONCLUSIONS AND DISCUSSION

A. Velocity autocorrelation function

In the important range of t, out to the first zero after the first minimum, the independent ion model with two adjustable parameters, expressed by Eq. (12), gives an excellent account of $\hat{Z}(t)$ for the three Rb states calculated by Mountain and Haan [19], and for the Na state calculated by Rahman [21].

From long experience with pseudopotential theory for simple metals [37,38], we are confident that these calculations [19,21] represent real liquid Rb and Na quite well. Further, in view of the similarity of the interionic potentials given for different metals by pseudopotential theory, we are confident that the independent ion model will give a good account of $\hat{Z}(t)$ for all nearly-free-electron metals. Still further, there is no obvious reason to doubt that the independent ion model will give a respectable account of $\hat{Z}(t)$ for liquid metals in general, with the probable exception of those exhibiting unusual configurational order in the liquid state, as reflected in their pair correlation functions [39], for example Sb, Bi, Si, and Ge. Finally, it is conceivable that the independent ion model will agree with computer calculations of $\hat{Z}(t)$ for compressed Ar, at say 1 kbar or so, where Ar appears to be more liquidlike [3,23,40].

B. Liquid and crystal frequencies

Liquid dynamics theory predicts, for normal melting elements, that the central moments (the 0, 1, and 2 moments) of the normal mode spectrum should be about the same for the liquid and crystal phases, at the same density [1]. The result in Table I for the alkali metals, that the liquid ω, determined from the velocity autocorrelation function, is nearly the same as the crystal ω_2, determined from inelastic-neutron-scattering phonon measurements, is a striking confirmation of this prediction. Again, there is no obvious reason to doubt that $\omega \approx \omega_2$ will hold for the elements in general, as long as liquid and crystal phases have approximately the same electronic structure, i.e., for normal melting.

C. Transit parameter ξ

The independent ion model provides Eq. (14) for $D(\omega,\xi)$. If we replace ω by ω_2, and use experimental data for ω_2 and D, the resulting curve of ξ vs T/T_m at atmospheric pressure is roughly universal for nine liquid metals, as shown in Fig. 3. The increase of ξ with T/T_m is expected, since the transit probability μ should increase weakly with T/T_m. Its universality encourages us to imagine that ξ is a useful physical parameter, especially since ω_2 varies by a factor of 6.6 for the liquid metals in Table II. Finally, among the ten normal-melting liquid metals for which we found sufficient data to analyze for ξ, mercury definitely falls outside the universal group in Fig. 3.

D. Transit probability μ

From Eqs. (4) and (5), ξ is a combination of the probability μ that an ion at a turning point will transit to a new well, and the change in direction θ of the ion's motion when the transit occurs. Though we have not evaluated these factors separately, it is clear from our results for ξ, Table I and Fig. 3, that μ is around $\frac{1}{2}$. This confirms the hypothesis of Sec. II, that each ion transits approximately once in the mean vibrational period τ, and such frequent occurrence of transit motion then provides the logical basis for the independent ion model, as argued in Sec. II.

Equilibrium liquid dynamics theory expresses the ion-motional specific heat of monatomic liquids as [1]

$$C_I = C_H + C_A + C_B, \tag{17}$$

where the quasiharmonic vibrational contribution $C_H = 3Nk$ is the dominant term, and C_A and C_B are anharmonic and boundary contributions, respectively. We have recently analyzed experimental data in terms of Eq. (17), and found the magnitudes and temperature dependences of C_A and C_B for liquid metals [3]. In comparison with the present study of nonequilibrium processes, we note the boundary specific heat C_B is precisely the equilibrium manifestation of the presence of transit motion, and the magnitude and temperature dependence of C_B is in qualitative agreement with the independent ion model having μ around $\frac{1}{2}$.

E. Zwanzig's model

Zwanzig [41] presented a model which, at a glance, looks quite similar to the present self-diffusion model, but is different in two crucial aspects. Zwanzig supposed that the atoms in a subvolume undergo harmonic oscillations about some equilibrium positions, then jump to new equilibrium positions, and that the net effect of the jump is to destroy coherence of the oscillations within the subvolume. The atomic motion is then written as a sum over harmonic modes about a fixed equilibrium configuration, times a factor $\exp(-t/\tau_w)$ to account for decoherence from the diffusive jumps, where τ_w is a waiting time. Hence, in Zwanzig's model, the diffusive jump itself is not included as part of the atomic motion. In addition, Zwanzig noted that his dynamical picture makes sense only if the waiting time τ_w is much longer than a Debye period.

By contrast, in our model, within the small volume of an ion and its near neighbors, diffusive jumps take place many times within a single Debye period. Second, in our independent ion model, the transits, which represent the diffusive jumps, are not omitted but are included as an essential part of the motion.

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