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FEATURE ARTICLE

Instantaneous Normal Mode Approach to Liquid State Dynamics

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The instantaneous normal mode (INM) approach to liquid state dynamics is presented. INM is put in historical context, and the underlying physical ideas, including the importance of the potential energy landscape, are explained. It is shown that INM can be the basis of a general starting point for dynamical calculations in liquids, and the theoretical developments necessary for future development are indicated. New results are given for the general INM formalism, as well as for depolarized light scattering, the "Boson peak" in supercooled liquids, friction on a vibrating bond, nonadiabatic solvent induced transitions of a quantum system coupled to a liquid, and diffusion in supercooled liquids.

1. History and Introduction

In this article we will discuss the approach to dynamics in liquids based upon "instantaneous normal modes" (INMs). INM theories provide a comprehensive point of view with great intuitive appeal and hold particular promise for supercooled liquid dynamics, for interpretation of ultrafast optical experiments, and for coupling of molecular internal degrees of freedom to a solvent bath.

The idea of finding normal modes in liquids is a natural one, given the success of that concept in solids and given Maxwell's suggestion[1] that liquids are solid-like at short times $t < \tau_M$. In supercooled liquids the Maxwell time τ_M increases strongly with decreasing T, and the appeal of the idea grows as well. Solid-like theories of liquids have fallen in and out of fashion since Maxwell, but the thread is continuous. We regard INM as its current manifestation, strongly influenced by Zwanzig's[2] investigation in 1967 of the possible existence of normal modes in liquids. Rahman, Mandell, and McTague[3] actually carried out an INM calculation on amorphous Lennard-Jones (LJ) in 1976. Although the system is not a liquid, it has a finite diffusion constant, and their work foreshadows many features of the current formalism: "... the presence of an apparently finite diffusion constant does not allow such a simple determination of the density of states. However by constructing the force constant matrix at any instant of time one can study not only the spectrum of real eigenvalues but that of the imaginary ones as well." Indeed, the INM are[4] the eigenfunctions of the force constant matrix from an "instant of time". The frequencies are the square roots of the eigenvalues, and the unaveraged density of states is

$$\rho(\omega) = \sum \delta(\omega - \omega_\alpha) \qquad (1.1)$$

Averaging eq 1.1 yields the INM density of states, $\langle \rho(\omega) \rangle$. Positive eigenvalues lead to the usual real frequencies, but the negative eigenvalues found in liquids give imaginary frequencies. The separate spectra of the real (stable) frequencies, $\langle \rho_s(\omega) \rangle$, and of the imaginary (unstable) frequencies, $\langle \rho_u(\omega) \rangle$, play key roles in INM calculations. Densities of states for the unit density, supercooled LJ liquid are shown in Figure 1. We use reduced units unless stated otherwise, and the contribution of the Im-ω modes is plotted on the negative real axis, $i\omega \rightarrow -\omega$; $\langle \rho_u(\omega) \rangle$ for positive ω means $\langle \rho_u(|\omega|) \rangle$.

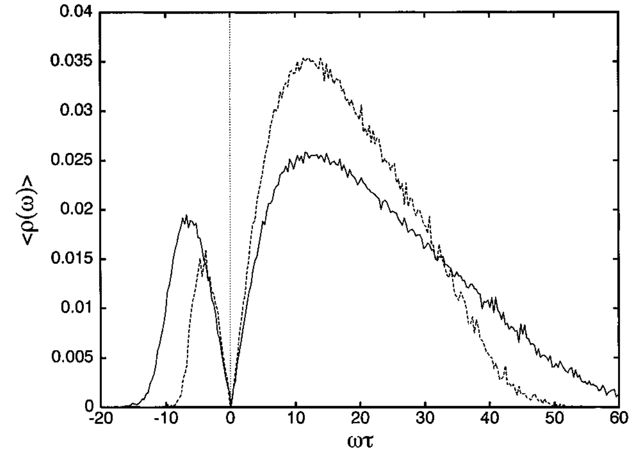

Figure 1. INM density of states vs $\omega\tau$ in supercooled unit density Lennard-Jones liquid at reduced temperatures, $T = 1.25$ (solid line) and $T = 0.50$; τ is natural LJ time, 2.18 ps for Ar. Note decreased unstable mode lobe at lower T.

In an atomic harmonic crystal the Fourier transform, $f(\omega)$, of the velocity correlation function, $C(t)$, is determined by the density of states, $\rho(\omega)$,

$$f(\omega) = T\,\rho(\omega) \qquad (1.2a)$$

$$C(t) = T\int d\omega\, \rho(\omega) \cos(\omega t) \qquad (1.2b)$$

Rahman et al. tested[3] eq 1.2a, replacing $\rho(\omega)$ with the INM density of states ($g(\omega)$ in their notation) and found excellent agreement with the simulated $f(\omega)$. By demonstrating a successful INM calculation of C(t) for a particular system, their work held out the prospect of a more generally applicable formalism. They further remark "... the smaller population of low frequency modes in $g(\omega)$ than in $f(\omega)$ is because $g(\omega)$ does not monitor all the relaxation processes inherent in this system." This statement is also significant. Truly dissipative relaxation

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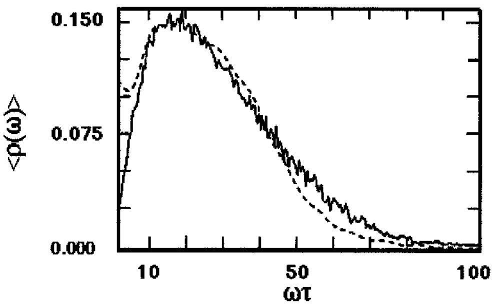

Figure 2. Normalized stable INM density of states (solid line) and $f(\omega)/T$ ($f(\omega)$ is transformed velocity correlation) vs $\omega\tau$ in supercooled LJ liquid, $T = 300$ K, $P = 10$ kbar.

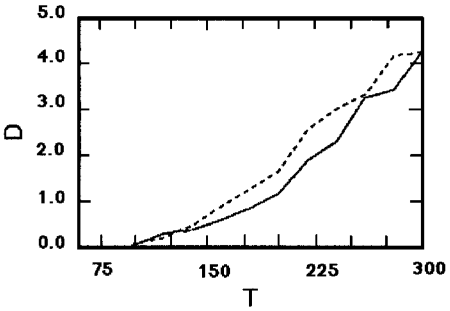

Figure 3. Prediction of eq 1.3 and simulated $D(T)$ (solid line) vs T in supercooled LJ, $P = 10$ kbar; units for D are $\text{cm}^2/\text{s} \times 10^5$.

processes must be added in to the INM starting point, an area of ongoing research.

Equation 1.2, with $\rho(\omega)$ replaced[5] by a normalized $\langle\rho_s(\omega)\rangle$ is perhaps the simplest INM result and demonstrates both the utility of, and challenges to be met in, the application of solid state thinking to liquids. The stable INM density of states vanishes at zero frequency, while $f(\omega{=}0)$ equals the self-diffusion constant, D, the integral of $C(t)$. Thus, the diffusion constant is predicted to vanish; furthermore, discarding the Im-ω modes and correspondingly increasing the area of $\langle\rho_s(\omega)\rangle$ is unjustified. These difficulties become less important with decreasing temperature, since $D \rightarrow 0$ and the "fraction of unstable modes", denoted f_u, decreases. When both D and f_u are small, eq 1.2a can be very accurate,[5] as seen in Figure 2.

The significance of the imaginary frequency modes is less clear than that of the stable modes. LaViolette and Stillinger,[6] and Cotterill and Masden,[7] suggested that the number of unstable modes might correlate with fluidity, and indeed D may be calculated from the imaginary frequency modes. The decrease in amplitude of $\langle\rho_u(\omega)\rangle$ with decreasing T shown in Figure 1 mirrors a decreasing fluidity. Figure 3 is a test of the INM formula[8]

$$D(T) = \text{const}\, \langle\omega_u\rangle\, f_u \qquad (1.3)$$

in LJ at $P = 10$ kbar, where $\langle\omega_u\rangle$ is the averaged unstable mode frequency. A related formula[9] is of comparable accuracy in supercooled CS_2, where, diffusion being a translational phenomenon, the fraction of translational unstable modes must be used.

To go beyond solid state formulas and qualitative correlations, a physical picture is essential. Goldstein[10] has formulated supercooled liquid dynamics in terms of the topology, or *landscape*, of the many-body potential surface, a viewpoint that is superbly attuned to INM. The liquid is described by interrupted harmonic dynamics, with periods of harmonic oscillation near the local minima (the wells)—"the liquid or glassy region has, unlike the portion associated with the crystalline solid, a large number of minima, of varying depths"—interrupted by barrier crossing—"As temperature is raised, sufficient thermal energy ... will become available to allow transitions to take place over potential barriers, even though they are large compared to the thermal energy." Weber and Stillinger[11] verified Goldstein's proposal via computer simulation; they found that the cold liquid remained in the wells for relatively long times and obtained ω_h, the barrier hopping rate. Zwanzig[12] used this idea to calculate the velocity correlation function, assuming harmonic dynamics in the wells and randomization upon barrier crossing; the result is

$$C(t) = T\int d\omega\, \rho_q(\omega) \cos(\omega t) \exp(-t/\tau) \qquad (1.4)$$

where $\tau = \omega_h^{-1}$ is the waiting time of the system in a well and $\rho_q(\omega)$ is the averaged spectrum of modes from the local minima, the "quenched normal modes" (QNM). One might suspect a relation between τ and the Maxwell time, τ_M, a point deserving further investigation. The QNM, which among other properties have all real ω, are not the INM, but eq 1.4 has now been applied with both,[13,14] and here we regard it as an INM formula. Equation 1.4 yields a finite diffusion constant, even with $\rho_q(\omega{=}0) = 0$.

Most of the basic ideas behind current INM calculations in liquids are present in the papers just discussed. The liquid forms relatively stable local structures (the local minima) which support harmonic dynamics, the stable INM with spectrum $\langle\rho_s(\omega)\rangle$. Structural relaxation corresponds to barrier crossing to neighbor wells, and introduces dissipation. Imaginary frequency modes (downward curvature of potential) are observable during barrier crossing only, and thus $\langle\rho_u(\omega)\rangle$ is a source of information about barrier crossing. In fact $\langle\rho_u(\omega)\rangle$ contains enough information to allow a calculation[15] of the barrier hopping rate and[16] the distribution of barriers to diffusion, $g(E)$. Thus, in a neat closed loop, the unstable modes yield the damping of the stable modes. Of course the idea that diffusion requires barrier crossing has a long history of distinguished practitioners, notably Eyring,[17] and is the obvious explanation for exponential T-dependence of $D(T)$. While $\langle\rho(\omega)\rangle$ is most often obtained numerically, analytic theories have been given by Stratt et al.[18] and by Wu and Loring.[19]

It is an oversimplification to state that all Im-ω modes correspond to barriers. We proposed[15] the existence of a cutoff ω_c such that for $|\omega| < \omega_c$ the modes were unrelated to barrier crossing. Bembenek and Laird[20] verified the existence of a cutoff by calculating the one-dimensional potential energy profiles $U(q)$. They showed that for $|\omega| < \omega_c$ the $U(q)$ are "shoulder (SH) potentials"—single-well potentials with inflection points on the shoulder—while for $|\omega| > \omega_c$ double-well (DW) barrier crossing profiles (plus SH contributions) appear. The cutoff may also be obtained[21] with analytical methods. We recently found that it is symmetric; for $\omega > \omega_c$, Re-ω modes are single-well (SW) harmonic oscillators, but for $\omega < \omega_c$ small SH contributions appear. Thus *harmonic* Im and Re frequency modes vanish and are depleted, respectively, for $|\omega| < \omega_c$, and this has very important consequences.

For times that are short compared to τ, barrier crossing may be ignored and time correlation functions calculated via textbook use of the stable INM. Unstable INM may also be employed carefully, although their time dependence is $\cosh(\omega t)$ which diverges at long times. From the eigenvectors it is possible to associate specific dynamical features with specific atomic or molecular motions. This is the basis of one of the two principal directions, broadly speaking, of INM theory and has been the subject of two reviews, by Stratt[22] and by Stratt and Maroncelli.[23] Many current experiments focus on the ultrafast time scale, so such theories are directly applicable. Again, τ increases as T decreases and the "short time" regime expands in supercooled liquids. Equation 1.2 is an elementary formula of this type.

The second principal direction is the construction of time correlation functions accurate at all times, following eq 1.4, with ω_h obtained from $\langle\rho_u(\omega)\rangle$. Integration leads to INM expressions for transport coefficients, e.g. the self-diffusion constant. This approach allows a new explanation[15,24,25] of the Arrhenius and stronger-than-Arrhenius T-dependence characteristic of strong and fragile supercooled liquids. Here the point is not that an accurate short time approximation is available from $\langle\rho_s(\omega)\rangle$, but that $\langle\rho_u(\omega)\rangle$ provides a sufficiently rich description of transport via barrier crossing to yield the long time decay, *if the cutoff* ω_c *is properly included*. Equations 1.3 and 1.4 belong to this class of INM result.

2. INM Theory of Time Correlation Functions

2a. General Considerations and Suggestions. We seek a theory of time correlation functions in which controlled, physically motivated approximations are generated in terms of the properties of the INM. Ultimately one would hope for a formally exact starting point. Two steps are indicated: first, an arbitrary dynamical variable must be expressed in terms of INM variables; second, the dynamics of those variables must be found. The INM themselves are well-defined dynamical variables. The eigenvectors $(\alpha,i;t)$ and the eigenvalues $\epsilon_\alpha(t)$ are functions, albeit unusually complicated ones, of the positions $r_i(t)$; Roman index denotes both particle number and Cartesian direction, Greek index denotes normal mode, and summation over repeated indices is implied. Natural INM position and velocity variables in atomic liquids are $\{q_\alpha, v_\alpha\}$

$$q_\alpha(t) = \sum(\alpha,i;t)\, r_i(t) \qquad v_\alpha(t) = \sum(\alpha,i;t)\, v_i(t) \tag{2.1}$$

and are related to familiar Fourier collective variables by the replacement $(\alpha,i;t) \rightarrow \exp(ik\cdot r_i)$. If possible we would like to avoid dealing with $q_\alpha(t)$, with its dependence on the absolute atomic positions which need not be small. More generally the INM are[22] linear combinations of mass-weighted coordinates, but the mass can be removed from many manipulations by incorporating it into the definition of reduced units.

Expression of the usual quantities as INM is straightforward for variables which are generalized velocities (odd functions of the velocity). Consider first the velocity correlation function. INM expansion of $v_i(t)$ in terms of the $v_\alpha(t)$ yields

$$C(t) = \langle v_i(t)\, v_i(0)\rangle = \sum\langle(i,\alpha;t)\,(i,\beta;0)\, v_\alpha(t)\, v_\beta(0)\rangle \tag{2.2}$$

Summing over i and dividing by $3N$ eliminates reference to a particular particle,

$$C(t) = \sum\langle \mathrm{d}(\alpha,\beta;t)\, v_\alpha(t)\, v_\beta(0)\rangle \tag{2.3}$$

$$\mathrm{d}(\alpha,\beta;t) = (1/3N)\sum(i,\alpha;t)\,(i,\beta;0) \tag{2.4}$$

At any instant the $(i,\alpha;t)$ obey the usual ortho-normality relations, $\sum(i,\alpha;t)\,(i,\beta;t) = \delta_{\alpha\beta}$. In a harmonic crystal these coefficients are time-independent, $\mathrm{d}(\alpha,\beta;t)$ reduces to $(1/3N)\delta_{\alpha\beta}$, $C(t) = (1/3N)\sum\langle v_\alpha(t)\, v_\alpha(0)\rangle$, and $\langle v_\alpha(t)\, v_\alpha(0)\rangle = T\cos(\omega_\alpha t)$. Were we to make all the harmonic approximations in a *liquid*, assume that Re-ω results can be applied to Im-ω by simply substituting $\omega \rightarrow i\omega$, and replace the sums over modes by integrals over the density of states, we would obtain

$$C(t) = T\int \mathrm{d}\omega\, [\langle\rho_s(\omega)\rangle \cos(\omega t) + \langle\rho_u(\omega)\rangle \cosh(\omega t)] \tag{2.5}$$

In liquids $\mathrm{d}(\alpha,\beta;t)$ is more complicated, and the dynamics of $v_\alpha(t)$ are not described by cos or cosh. Nevertheless we have an expression where the harmonic limit is evident and where liquid-like behavior enters through INM variables. The harmonic approximation is a good one in liquids at short times, and the time expansion of eq 2.5 yields[13,14] the exact t^2 and t^4 terms.

Cho and Stratt[26] showed how to apply the above ideas to any generalized velocity variable $\mathrm{d}A/\mathrm{d}t$ which is the time derivative of a generalized position A (even function of the velocities). For a configuration close to that at which the INM were found, A is expanded

$$A(t) = A(0) + \sum(\mathrm{d}A/\mathrm{d}q_\alpha)\, \mathrm{d}q_\alpha \tag{2.6}$$

where $\mathrm{d}q_\alpha$ is (eq 2.1) q_α with $r_i(t)$ replaced by $r_i(t) - r_i(0)$. The reference to the expansion point drops out of the time derivative

$$\mathrm{d}A(t)/\mathrm{d}t = \sum(\mathrm{d}A/\mathrm{d}q_\alpha)\, v_\alpha \tag{2.7}$$

and one can write down the correlation function, having introduced the derivatives of the physical variable with respect to the INM.

A fundamental dynamical quantity, the time derivative of the force on a particle, has a special relation to the INM. From the harmonic expansion of the potential

$$F_i(t) - F_i(0) = \sum(i,\alpha;0)\, \epsilon_\alpha(0)\, [q_\alpha(t) - q_\alpha(0)] \tag{2.8}$$

Setting $t = \delta t$, $\delta t \rightarrow 0$ and dividing both sides by δt yields

$$\mathrm{d}F_i/\mathrm{d}t = \sum(i,\alpha;t)\, \epsilon_\alpha\, v_\alpha \tag{2.9}$$

The diffusion constant may be calculated from the integral of the $\mathrm{d}F/\mathrm{d}t$ correlation function as well as from the velocity correlation. That observation has been[27] the basis of mode-coupling theories of tagged particle motion in liquids; $\mathrm{d}F/\mathrm{d}t$ is in some ways a better starting point. Equation 2.9 easily yields an INM expression for the $\mathrm{d}F/\mathrm{d}t$ correlation. Thus we have expressed two important correlation functions using INM variables.

For generalized positions Cho and Stratt[26] suggested that the time correlation function be expressed as the double time integral of the $\mathrm{d}A/\mathrm{d}t$ correlation, where $\mathrm{d}A/\mathrm{d}t$ is a velocity, and that a purely harmonic INM approximation be applied to $\mathrm{d}A/\mathrm{d}t$; thus

$$\langle\delta A(t)\, \delta A(0)\rangle = [\langle(\delta A)^2\rangle - \int \mathrm{d}\omega\, (T/\omega^2)\langle\rho^A(\omega)\rangle] + \int \mathrm{d}\omega\, (T/\omega^2)\langle\rho^A(\omega)\rangle \cos(\omega t) \tag{2.10}$$

where $\delta A = A - \langle A\rangle$ and Im-ω modes may be included for short times with $\cos(i\omega t) = \cosh(\omega t)$. The weighted INM density of states is[26]

$$\langle\rho^A(\omega)\rangle = \langle\sum(\mathrm{d}A/\mathrm{d}q_\alpha)^2\, \delta(\omega - \omega_\alpha)\rangle \tag{2.11}$$

Equation 2.10 has been extensively employed[22,23] in the interpretation of solvation experiments, where A is the solvation energy. It is analogous to eq 2.5 in that it assumes harmonic dynamics and thus has not yet dealt with some of the complications involved in an INM theory of liquids. Among other things, it does not decay to zero at long time. Nonetheless eq 2.10 is, like eq 2.5, accurate at short time. The solvation studies by Stratt, Maroncelli, and Ladanyi demonstrate[22,23,28] the capability of INM, through the eigenvectors, to isolate the detailed molecular motions corresponding to particular dynamical features. If the variable A is a short ranged function of its argument, $\langle \rho^A(\omega) \rangle$ is well-described by a particularly simple analytic approximation.[29]

We proposed[30] to deal directly with coordinate correlation functions using eq 2.6 and the physical picture of the system hopping among the many-body potential wells. Harmonic dynamics are assumed to hold while the system is in a given well, and the correlation function is calculated for that well (denoted by brackets)

$$[\delta A(t)\ \delta A(0)] = \delta A_w^{\ 2} + \int \mathrm{d}\omega\ (T/\omega^2)\ \rho_w^{\ A}(\omega) \cos(\omega t) \tag{2.12}$$

where the harmonic result, $\langle q_\omega^{\ 2} \rangle = T/\omega^2$, has been employed. $\delta A_w = A_w - \langle A_w \rangle$ and A_w is the average value in the well. The notable feature of eq 2.12 is the constant $\delta A_w^{\ 2}$; the harmonic fluctuations are about a nonzero value in the well, and harmonic dynamics will not relax this part of A. However, hopping among the wells will change and randomize A_w, as well as relaxing the harmonic oscillations. Averaging over the ensemble of wells and introducing hopping,

$$\langle \delta A(t)\ \delta A(0) \rangle / \langle (\delta A)^2 \rangle = [(1 - F_H) + F_H \int \mathrm{d}\omega\ (T/\omega^2)\ \langle \rho^A(\omega) \rangle \cos(\omega t) / (\int \mathrm{d}\omega\ (T/\omega^2)\ \langle \rho^A(\omega) \rangle)] \exp(-t/\tau_A) \tag{2.13}$$

where the *harmonic fraction* is $F_H = \int \mathrm{d}\omega\ (T/\omega^2)\ \langle \rho^A(\omega) \rangle / \langle (\delta A)^2 \rangle$. Equation 2.13 is identical to the Cho−Stratt equation except, with damping added, it decays to zero at long time. Hopping may relax different dynamical variables with different rates (τ_A), and of course mode and ω-independent exponential damping is only a first approximation. While this heuristic derivation is not identical to that of Cho and Stratt, it may explain why eq 2.10 does not decay at long time; harmonic dynamics in the wells cannot, and should not, relax that part of the fluctuations due to barrier crossing or structural relaxation. In our view barrier crossing corresponds to the slow "α" process of liquids, while harmonic dynamics in the wells is a fast "β" process. Thus INM allows[30] a new perspective on the phenomenon of α/β relaxation.

We have used eq 2.13 to calculate the polarizability correlation function,[30] and Rayleigh/Raman scattering,[31] in CS_2. The relevant density of states is weighted by the squares of the derivatives $\mathrm{d}\Pi^{(2)}/\mathrm{d}q$ and $\mathrm{d}\Pi^{(0)}/\mathrm{d}q$ for anisotropic and isotropic scattering, respectively, τ_π is taken to be the second-rank rotational diffusion time, and we used the normalized $\langle \rho_s^{\ \Pi}(\omega) \rangle$. The nonharmonic contribution provides a new interpretation of the narrow line in the anisotropic Rayleigh spectrum. Agreement with simulation is excellent, with separate fast and slow processes clearly visible at the freezing point, 165 K. The simulation includes molecular vibrations, which are in reality quantum mechanical; thus we,[31] and others,[32] have given a method for quantum correction of classical INM. In addition we decompose the densities of states into contributions from translations parallel and perpendicular to the molecular axis, and rotations; this is shown for the anisotropic $\langle \rho^{\Pi 2}(\omega) \rangle$ in Figure 4. The trans-|| piece, away from $\omega = 0$ resembles the spectrum in simple liquids, an exponential decay, while the rotations appear to have more of a distinct peak (all parts of $\langle \rho^{\Pi 2}(\omega) \rangle$ vanish at $\omega = 0$). Interestingly, one empirical fit[33] to experimental data consists of a term $\omega \exp(-\omega/\omega_0)$ plus an antisymmetrized Gaussian peaked at a finite ω; INM may provide a physical basis for the fit. Comparison of the anisotropic and isotropic $\langle \rho^{\Pi}(\omega) \rangle$ yields a frequency-independent depolarization ratio of 0.69, in agreement with Simon's value[34] of 0.7 ± 1. INM polarizability calculations on acetonitrile have been performed[35] by Ladanyi and Klein, with an alternative mode decomposition.

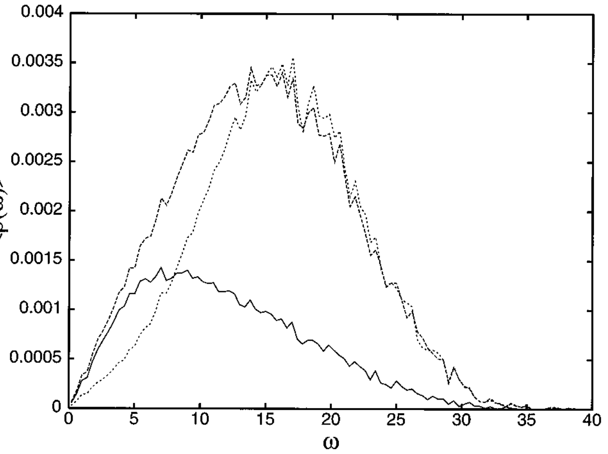

Figure 4. Anisotropic polarizability INM density of states vs ω (ps^{-1}) for CS_2 at 165 K, decomposed into distinct physical components. Translation parallel to the molecular axis (solid line), perpendicular translation (heavy dashes), and rotations (light dashes) are represented.

The question of how to obtain INM dynamics remains. Time correlation functions of the INM variables could be obtained via approximations to an exact starting point, or via intuitive modeling. We will now briefly suggest how one might go about rewriting the laws of motion so that INM approximations could be systematically constructed, and we will then cover modeling in more detail.

Mori's formalism[36] is exact for time correlation functions of an arbitrary set of dynamical variables, and is one of the cornerstones of dynamical theory in liquids. A microscopic derivation of hydrodynamics is obtained by choosing the number, momentum, and energy densities as the set of variables; it is not unreasonable that use of the INM variables would also lead to useful results. A more direct route is possible, based on the expression of $\mathrm{d}F/\mathrm{d}t$ by INM. The time derivative of $a_\alpha \equiv (\mathrm{d}v_\alpha/\mathrm{d}t)$ contains $\mathrm{d}F/\mathrm{d}t$ and first and second derivatives of $(i,\alpha;t)$. Eliminating $\mathrm{d}F_i/\mathrm{d}t$ with eq 2.9 yields closed coupled equations for $v_\alpha(t)$ and $a_\alpha(t)$ containing the INM quantities as time-dependent coefficients

$$\mathrm{d}v_\alpha(t)/\mathrm{d}t = a_\alpha(t) \tag{2.14}$$

$$\mathrm{d}a_\alpha(t)/\mathrm{d}t = \sum[\epsilon_\beta(t)\ \delta_{\alpha\beta} + \sum(\mathrm{d}^2(\alpha,i;t)/\mathrm{d}t^2)(i,\beta;t) - 2\sum c(\alpha,\gamma;t)\ c(\gamma,\beta;t)]\ v_\beta(t) + 2\sum c(\alpha,\beta;t)\ a_\beta(t) \tag{2.15}$$

where $c(\alpha,\beta;t) = \sum(\mathrm{d}(\alpha,i;t)/\mathrm{d}t)(i,\beta;t)$.

In each eigenanalysis, the modes are ordered by ω only, and it is not immediately obvious which mode at a previous time is the "ancestor" of a particular contemporary mode. Adiabatic INM (AINM) may be obtained[37] by identifying a mode at time t as the descendant of the mode at $t - \Delta t$, for $\Delta t \rightarrow 0$, with which it has the maximum overlap. The frequencies of the AINM do not cross,[37] so modes can simply be tracked by their ordering in ω. AINM may serve as a time-dependent "basis set", but note that the existence of an adiabatic basis does not imply adiabatic dynamics. Energy put into a single AINM at $t = 0$ will find its way into other AINM, with mixing particularly pronounced at the avoided crossings (AX). Alternate time-dependent INM are diabatic INM (DINM) which do cross at the AX of the AINM. Mode following will have to be incorporated into any INM formalism. Solving these equations is not a simple matter; they are nothing but a rewriting of Newton's equations. However they have a transparent harmonic oscillator limit when all the INM coefficients are time-independent. It should be possible to find perturbative solutions when the time derivatives are small. Equations 2.14 and 2.15 could form the beginning of systematic INM theory.

2b. Modeling of Correlation Functions: The Velocity Correlation. Consideration of the velocity correlation function illustrates the diversity of ideas arising from a very simple INM exercise. Equation 2.3 suggests that the time-dependent eigenvectors are the source of the damping of the INM, so we write

$$C(t) \equiv T\sum \mathrm{d}(t;\alpha)\, C(t;\alpha) \approx T\sum[(1/3N)\sum\langle(i,\alpha;t)(i,\alpha;0)\rangle]\, C(t;\alpha) \quad (2.16)$$

where $\langle v_\alpha(t)\, v_\alpha(0)\rangle = TC(t;\alpha)$. The first equality is our *definition* of a mode-dependent damping factor, $\mathrm{d}(t;\alpha)$. The second is an approximation obtained from eq 2.2 by factorizing the average, dropping the $\alpha \neq \beta$ terms and averaging over the equivalent atoms; $\mathrm{d}(t;\alpha)$ is then given by the eigenvector correlation function. The velocity correlation $C(t)$ may be constructed from the velocity correlation functions of individual modes and a function describing the lifetime of mode α, $\mathrm{d}(t;\alpha)$; the sum contains the imaginary frequency modes.

It is appealing that the mode lifetime be given by the eigenvector correlation. If[12] modes are randomized when the system hops to a neighbor potential well, it makes sense that the eigenvectors in the new well are decorrelated from the original vectors. However, one must be very careful approximating eq 2.2. At AX the AINM exchange identity, leading to a rapid decay of the eigenvector correlation function. The modes have simply been relabeled and $C(t)$ has not decayed, but this is not handled properly in the diagonal/factorization approximation. Thus the approximate eq 2.16 is expected to be innacurate for AINM, although it will be worth trying with the DINM which do cross and lack the peculiar randomization at avoided crossings of the AINM. Knowledge of the time evolution of the eigenvectors, over and above their relevance to eq 2.16, will help develop and verify the underlying INM ideas of harmonic oscillation, hopping, and randomization.

Were we to (1) replace $\mathrm{d}(t;\alpha)$ with $\exp(-t/\tau)$, a mode-independent decay, (2) discard the imaginary frequencies, and (3) assume that $C(t;\alpha)$ has the simple harmonic form, $\cos(\omega_\alpha(t{=}0)\,t)$, we would have something very close to eq 1.4. Extensions of the theory are possible in all three directions. Equation 2.16 explicitly contains mode-dependent damping as well as a prescription for inclusion of the imaginary frequency modes. Furthermore, $C(t;\alpha)$ need not equal $\cos(\omega_\alpha(t{=}0)t)$ or $\cosh(\omega_\alpha(t{=}0)t)$. The frequency of a mode may wander in time; such wandering causes motional narrowing,[38] a well-known phenomenon in vibrational spectroscopy, which has not previously been incorporated into intermolecular dynamics.

We first consider the case of fixed ω_α and examine what can be done with points (1) and (2); thus,

$$C(t) = T\,[\int \mathrm{d}\omega\, \langle\rho_s(\omega)\rangle\, \mathrm{d}_s(t;\omega)\cos(\omega t) + \int \mathrm{d}\omega\, \langle\rho_u(\omega)\rangle\, \mathrm{d}_u(t;\omega)\cosh(\omega t)] \quad (2.17)$$

The presence of imaginary frequency modes is significant for the development of INM theory. Because the cosh grows exponentially at long times, direct contributions of Im-ω modes have been limited to short time so far, the exception being a calculation[39] of friction where a short lifetime "tames" their contribution. Similarly, in eq 2.17, decay of $\mathrm{d}_u(t;\omega)$ can cause the unstable contribution to be well-behaved. The case for inclusion of unstable modes is compelling because[13] eq 2.17 then yields the correct time expansion to t^4 *if* the leading term in the time expansion of $\mathrm{d}(t;\omega)$ is t^6 or higher. This is an unusually flat function at short time, and it will be very interesting to see how $\mathrm{d}(t;\omega)$ finally turns out. Recall also that in eq 2.13 we suggested exponential damping for a coordinate correlation function, but only as a first approximation. The undamped eq 2.13 is exact to t^2, so the damping must have a leading term of t^4. Apparently the damping functions describe *purely* slow processes; if damping is due to rotation, it is the long time part of rotation, not fast librations.

Analytical methods may be used to obtain the damping. In ref 15 we used $\langle\rho_u(\omega)\rangle$ to calculate an ω-independent averaged exponential decay rate, ω_h, for the stable modes. That rate was an average over barriers with all different frequencies. If a barrier with a given ω connects to a stable coordinate with about the same ω in the adjoining well,[40] the barriers at ω could be used to damp the stable modes at ω for ω-dependent damping. A decay time for the unstable modes should be the lifetime, τ_u, of the system on a barrier. In the simplest one-dimensional model, $\tau/\tau_u = P_s/P_u = f_s/f_u = (1 - f_u)/f_u$, where P_s and P_u are the probabilities of being in a well and on a barrier. Vijayadamodar and Nitzan proposed[40] an ω-dependent version

$$\exp(-\beta E(\omega)) \approx \tau_u(\omega)/\tau(\omega) = \langle\rho_u(\omega)\rangle/\langle\rho_s(\omega)\rangle \quad (2.18)$$

and obtained good results for diffusion in normal liquid, unit density LJ with the Zwanzig theory. It will not be difficult[15] to treat multidimensional barriers. An exponential decay is not desirable, but these are the first steps to a theory of $\mathrm{d}(t;\omega)$. Fourkas et al. have proposed[41] a novel ω-dependent lifetime in a quantum INM interpretation of their RIKES experiments.

The INM, while found with a harmonic analysis, may not display harmonic dynamics. We consider two manifestations of this possibility. Firstly[20,21] for $|\omega| < \omega_c$ the Im-ω modes are "shoulder modes", and the Re-ω modes have a shoulder contribution; it is unlikely that the harmonic time dependences, cos or cosh, apply. For a harmonic INM theory it is plausible[15,25] to simply put a lower cutoff on the integrals in eq 2.17, or better, use[20] densities of SW and DW modes.

We will then be calculating a particular INM *contribution* to a time correlation function; what is the remainder? The dynamics of SH modes are bound up with the question of the relation of INM to hydrodynamics, which governs the largest length, longest time, decay in liquids. Hydrodynamic modes might be expected to appear as damped, delocalized "phonons" in INM calculations. INM phonons have not been found, although there exists[42] some evidence of large scale INM cooperativity. It is possible, then, that the SW and DW INM are local modes in liquids, which must be supplemented by the hydrodynamic modes at $|\omega| < \omega_c$ for a complete description. We have pursued[21,24] Bucheneau's suggestion[43] that the INM could be the liquid version of the "soft potential modes" used[43] in the theory of glasses. The SH modes may be the INM connection to hydrodynamics. Both $\langle\rho_s(\omega)\rangle$ and $\langle\rho_u(\omega)\rangle$ are $\sim\omega$ at low ω, which we have argued[24] is a possible consequence of long ranged disorder. It could also be said that the linear behavior is a consequence of the SH modes, thus linking them to long ranged excitations. Completing the SW/DW description with hydrodynamics could yield an INM velocity correlation with the correct "long time tails".[44]

INM time correlation functions are very sensitive to a lower cutoff. The Boson peak[45-48] is a low-ω peak seen in light and neutron scattering in supercooled liquids. At times before

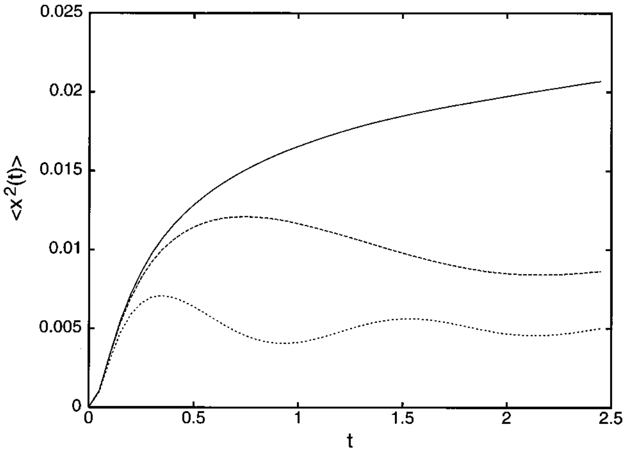

Figure 5. Mean square displacement, $\langle x^2(t)\rangle$ vs t (LJ units) at intermediate time for supercooled LJ liquid just above the glass transition with no cutoff (solid line), $\omega_c = 2$ (heavy dashes), and $\omega_c = 5$ (light dashes).

diffusion sets in, the mean square displacement, $\langle \delta x^2(t)\rangle$, rises from zero to a plateau. The strength of the Boson peak has been related[45,46] to the amplitude of an initial overshoot of the plateau by $\langle \delta x^2(t)\rangle$. Figure 5 shows $\langle \delta x^2(t)\rangle$ for unit density LJ at the glass transition as a function of cutoff. For no cutoff there is no overshoot; for $\omega_c = 5$, our[15] rough estimate, there is a marked overshoot. We are not saying that LJ has a Boson peak, only demonstrating the role of a cutoff. *We predict that the strength of the Boson peak correlates with* ω_c. Note also that INM correlation functions of coordinates are written as frequency integrals with integrands containing the factor T/ω^2, the harmonic formula for $\langle q_\omega{}^2\rangle$. Since $\langle \rho(\omega)\rangle \approx \omega$, $\omega \rightarrow 0$, a badly behaved integrand can result, a difficulty which is removed by a cutoff. It will also be valuable to obtain the true behavior of $\langle q_\omega{}^2\rangle$ for nonharmonic INM.

Because we have already[15,24,25] correlated the T-dependence of relaxation times with ω_c, structural relaxation and the[48] "mesoscopic" (intermediate time) dynamics of supercooled liquids are implicitly interrelated by INM theory in the Boson peak calculation. Such relations[45−48] are a topic of current interest. Sokolov[48] outlines a view of supercooled dynamics in which there are two contributions to mesoscopic dynamics, "an anharmonic relaxation-like contribution which is traditionally ascribed to motion in double wells" and "harmonic quasi-local vibrational excitations, which show up as the low-frequency so-called Boson peak"; the mesoscopic dynamics, remarkably, correlates with structural relaxation 10 orders of magnitude slower. The excitations invoked for mesoscopic dynamics are explicitly realized as the DW and SW INM, respectively, and the correlation with structural relaxation is seen in the INM calculation of ω_h from their densities of states.

A second source of nonharmonic dynamics is time-dependent frequencies. Zwanzig's picture[12] is of harmonic oscillators with fixed frequencies in one well becoming randomized by hopping. But if the frequencies fluctuate in a single well, the problem becomes analogous to calculations[38] of spectral lines, where fluctuating frequencies cause motional narrowing and relaxation via dynamic dephasing. For time-dependent frequencies

$$C(t;\alpha) = \langle \cos[\textstyle\int dt'\ \mathrm{Re}(\omega_\alpha(t'))]\ \cosh[\textstyle\int dt'\ \mathrm{Im}(\omega_\alpha(t'))]\rangle \tag{2.19}$$

in contrast to $\cos(\omega_\alpha t)$ or $\cosh(\omega_\alpha t)$. Equation 2.19 is the starting point for the Kubo[49] theory of spectral line shapes. It may be evaluated via simulation, or[49] by a cummulant expansion, characterized by the correlation function of the fluctuating frequency. Combination of eqs 2.19 and 2.16 yields a theory of the velocity correlation including Im-ω modes, ω-dependent damping, additional damping from dephasing, and motional narrowing. We hope that it serves as a framework for new approaches to dynamics in liquids.

2c. Internal Degrees of Freedom. Molecular vibrations are often well-described by the harmonic approximation. In liquids coupling of these modes to the bath is of the essence, and a harmonic INM description of the bath is ideally suited for coupling to harmonic intramolecular modes. The bath has been successfully modeled as[50] "Brownian oscillators"; using the INM to describe the Brownian oscillators could be a valuable synthesis. While classical theory and simulation may always be compared, real molecular vibrations are quantum mechanical. Fortunately, in another INM advantage, harmonic systems are the easiest to quantum correct.

Schvaneveldt and Loring[51] have used the Wu−Loring theory[19] to calculate the Fourier transform of the bond velocity correlation function, $C_V(\omega)$, which is related to the absorption spectrum, for a diatomic in various solvents. They obtain an INM expression for the bond friction, $\Gamma(\omega)$. To a first approximation the line width equals $\Gamma(\omega_V)/2$, where ω_V is the vibrational frequency. The friction is the Fourier transform of the correlation function of the random force on the bond and has been calculated[52] by Stratt et al. with INM for a rigid bond and by Schvaneveldt and Loring.[51]

INM vibrational lines can be[31,51,53] broader than the true lines. This, we believe, is a consequence of the absence of motional narrowing in existing theories. INM automatically includes inhomogeneous broadening, so competing effects must be included also. Equation 2.19 contains motional narrowing and is a promising route to this end. It is also desirable to see how the competition between motional narrowing and inhomogeneous broadening appears from the viewpoint of the friction. The friction determines the entire line shape, so every physical effect must have its counterpart therein.

Equation 2.13 is applicable to the time-dependent friction, with "A" = F^*, the random force on the bond; random means projected orthogonal to the bond coordinate. Considering a single molecule in solution, evaluation of $\langle \rho^{F^*}(\omega)\rangle$, the "random force density of states", is all that is required. For a rigid bond, $F = F^*$, the only modes are bath modes, and good results are obtained[52] for the "intermolecular" friction.

A vibrating diatomic, e.g. also has a "system mode", denoted ν, which is the bond stretching in an isolated molecule but which includes coupling to the bath in the liquid. The bond coordinate is not an INM in the liquid; it approaches an INM when the vibrational frequency ω_V is much larger than the highest intermolecular frequency (weak coupling), and it is a strongly coupled linear combination of several INM when ω_V lies within the continuum of intermolecular modes (strong coupling). The system mode survives the projection orthogonal to the bond in F^* to the extent that it is coupled to the bath. The orthogonality of the INM make taking the projection particularly easy, and we find,[54] for a given configuration in the weak coupling limit,

$$F^* = -\omega_\nu{}^2 \sum (b,\alpha)\ q_\alpha - \omega_\nu{}^2\ \epsilon\ q_\nu + F^a \tag{2.20}$$

where (b,α) is shorthand for the projection of bath mode α on the bond, $\epsilon = [(b,\nu)^{-2} - 1]$ is[54] a small coupling parameter, and F^a is the anharmonic part of the intramolecular potential. If the bond is identical to the system mode (zero coupling), $(b|\nu) = 1$ and $\epsilon = 0$. The anharmonic force appears because the Mori projection removes only the harmonic intramolecular contribution.

The first term on the right hand side of eq 2.20 contains energy relaxation from harmonic coupling to the bath; it is restricted to intermolecular frequencies and makes essentially no contribution to the line width if ω_V is outside the continuum. The second term might give inhomogeneous broadening. Since it is proportional to the system mode its contribution to $\Gamma(\omega)$ is always centered around ω_V, and it always contributes to $\Gamma(\omega_V)$. The anharmonic force broadens the line because a bond with an anharmonic potential samples a distribution of ω. An INM description of an anharmonic force would require higher order expansions in the q. There is, however, a good argument for ignoring F^a altogether. A quantum anharmonic oscillator still has just a single ground state and a single first excited state. If T is low enough that only the $0 \rightarrow 1$ transition is observed, there exists a single quantum frequency. The classical distribution of frequencies, and the corresponding presence of F^a in F^*, may[56] be regarded as classical artifacts.

Now consider damping of the INM friction time correlation function. Damping will broaden the system mode peak in $\Gamma(\omega)$ and reduce its amplitude at $\omega \approx \omega_V$, reducing the line width. Thus, the undamped system mode represents the full inhomogeneous broadening, and damping could introduce the competing effect of motional narrowing. Damping of the bath modes will also change the energy relaxation contribution to $\Gamma(\omega)$. In sum, the competing physical contributions to vibrational relaxation are visible in the INM friction.

More generally, time-dependent perturbation theory may be set up with INM ideas. The Hamiltonian for a solute is written as a sum of a molecular part, which contains the kinetic energy operator(s), and a solute−solvent interaction, $H = H^{mol} + V(R,\{r\})$, where R denotes the solute internal coordinate(s) and $\{r\}$ the solvent coordinates. The interaction V is expanded about the instantaneous configuration

$$V(R,\{r\}) = V(R,\{r^0\}) + \sum (\partial V(R,\{r\})/\partial q_\alpha)^0\, q_\alpha(t) \qquad (2.21)$$

and we write $H^0 = H^{mol} + V(R,\{r^0\})$, $H'(t) = \sum(\partial V(R,\{r\})/\partial q_\alpha)^0\, q_\alpha(t)$. If H^{mol} describes a two-level system, we can use perturbation theory for the transition rate R of solvent-induced level hopping between the eigenstates of H^0 in a given well, average the quantum harmonic (brackets) q correlations, and finally take a configuration average (angled brackets)

$$R = \hbar^{-2}\langle \rho^{(10)}(\omega_{10})\, [q^2](\omega_{10})\rangle \qquad (2.22)$$

where $\langle \rho^{(10)}(\omega)\rangle$ is a quantum mechanical weighted density of states with the contribution of each mode q weighted by

$$W_q(10) = \langle 1|(\partial V(R,\{r\})/\partial q)^0|0\rangle^2 \qquad (2.23)$$

and we use the Dirac notation for the initial ($|0>$) and final ($|1>$) states. Note that ω_{10} is within the average; the level spacing depends on the configuration since H^0 contains $V(R,\{r^0\})$. Equations 2.22 and 2.23 are applicable to nonadiabatic state hopping of electrons in liquids,[57] or might be applied directly to vibrational relaxation.

2d. Unstable Modes, Barrier Crossing, and Relaxation. The Im-ω density of states contains information about the barriers to diffusion which has formerly been unaccessible. A simple model[15] yields

$$\langle \rho_u(\omega,T)\rangle = (\alpha/3z)\, S(\omega,T)\, [1 + \int d\omega S(\omega,T)]^{-1} \qquad (2.24a)$$

$$S(\omega,T) = (s/m)\, n_V(\omega)\, G(\omega,T) \qquad (2.24b)$$

where $n_V(\omega)$ is the configuration-space volume weighted density of barriers and $G(\omega,T) \equiv \langle \exp(-\beta E)\rangle(\omega)$ is the *averaged Boltzmann factor* at ω. The parameters are α, number of coordinates with downward curvature at a barrier top; z, number of atoms in a cooperative[58] region (localization of INM); s, number of barriers connected to a minimum; m, number of minima connected to a barrier. In short, $\langle \rho_u(\omega,T)\rangle$ depends upon the topology—via $n_V(\omega)$ and the parameters—and upon the probability that the system has the thermal energy to visit a barrier at ω, governed by $G(\omega,T)$. The averaged Boltzmann factor is the most interesting part of $\langle \rho_u(\omega,T)\rangle$ and is our INM “window” on the potential energy landscape.

Consider the averaged hopping rate, ω_h. Given an expression, e.g. transition state theory (TST), for the rate of crossing a specific barrier, it is necessary to perform an average over all possible escape routes from a well. If this average is organized by contributions from barriers with different ω, an ω-integral results whose integrand contains the same quantities as those appearing in $S(\omega,T)$. The $d = 1$ TST rate is $k_{TST} = 1/(2\pi)\, (\omega/\omega_s) \exp(-\beta E)$, where ω_s is the frequency at the minimum. The exponential in k_{TST}, averaged over the distribution of heights of barriers with ω, is $G(\omega,T)$. Extending TST to $d > 1$ and completing the average we obtain[15]

$$\omega_h = m/(2\pi)\int d\omega\, \omega\, S(\omega,T) = m[(\alpha/3z) - f_u]^{-1}\int d\omega\, \omega \langle \rho_u(\omega,T)\rangle \qquad (2.25)$$

everything in eq 2.25 except the parameter m is available from $\langle \rho_u(\omega,T)\rangle$. It may be possible, as mentioned earlier, to relate the integrand of eq 2.25 to an ω-dependent decay rate, leading to better approximations to time correlation functions. One signature of supercooled liquids is[45,59] the stretched exponential decay of correlation functions, $C(t) = \exp[-(t/\tau)^\beta]$, which is thought[59] to arise from a distribution of decay times. If that distribution corresponds to the distribution of barrier curvatures, INM could yield a theory of the stretched exponential.

We have determined[15] the ω,T-dependence of $\langle \rho_u(\omega,T)\rangle$ in unit density supercooled LJ for $1.25 > T > 0.42$ (melting $T_M \approx 1.8$)

$$\langle \rho_u(\omega,T)\rangle = a(T)\, \omega \exp(-c\omega^4/T^2) \qquad (2.26)$$

and $c = 0.000\,20$. The exponential in eq 2.26 is, within a multiplicative constant, the averaged Boltzmann factor. Using eqs 1.4, 2.25, and 2.26 and taking the $\omega_h \rightarrow 0$ limit, appropriate for deeply supercooled systems, yields

$$D/T = 0.0068mT^{3/2} \qquad (2.27)$$

For the simplest case of $d = 1$ barriers, $m = 2$, the resulting[15] $D(T)$ is shown, along with simulation data, in Figure 6. We have, with no adjustable parameters, a quantitatively accurate theory for D in supercooled liquids, a theory of a completely new type.

One of the most important issues in supercooled liquids is[10,17,45,48,60] the microscopic origin of the ubiquitous “activated” exponential temperature-dependence of transport coefficients and relaxation times. Liquids whose exponential T-dependence follows an Arrhenius $\exp(-E/T)$ law all the way down to the glass transition at T_G have been named[45] “strong” liquids, while liquids which show a transition from Arrhenius to stronger T-dependence are “fragile” We have just calculated a $D(T)$ which is power law, no activated behavior at all. However the power law has arisen from an ω-integral of a density of states which, at a given ω, has one of the principal stronger-than-Arrhenius forms, the Zwanzig−Bassler[61] (ZB) $\exp(-E^2/T^2)$, with $E(\omega) = c^{1/2}\,\omega^2$.

This observation leads to an INM explanation of activated behavior. Relaxation arises as a sum of contributions from a distribution of barriers, organized according to ω. *Nothing can be understood* without consideration of the distribution of barrier heights; fluctuations are large, and replacing E with $\langle E\rangle$ will lead to *qualitatively* incorrect results. A single barrier gives Arrhenius dependence, but such behavior integrated over a smooth distribution of barrier heights easily collapses to a power law. What is required in the distribution so that activated behavior survives? A sharply peaked distribution would suffice, but more likely, we think, is one with a *lower cutoff*—an $E_{\min}$ below which the distribution of barriers falls off sharply. Since $E \approx \omega^2$, the energy and frequency cutoffs are related. Equation 2.25 should contain the lower frequency cutoff, including only DW modes and leading to the expression[15]

$$D/T = 0.0068mT^{3/2}\exp(-c\omega_c^{\,4}/T^2) \tag{2.28}$$

i.e. INM-derived ZB behavior. At the lowest temperatures in Figure 6 the data fall below the no-cutoff theory; eq 2.28 fits those points with $\omega_c = 4.54$. Physically, a lower cutoff is required because otherwise, at any T, there exist enough barriers with $E < T$ which can be crossed without activation. Activation energies in Arrhenius or ZB expressions are representative of $E_{\min}$, not of the average barrier energy.

It has become apparent[25,40] that $\langle\rho_u(\omega,T)\rangle$ changes from ZB to an Arrhenius $\exp(-c'\omega^2/T)$ law at a crossover temperature $T_{\mathrm{Fl}} > T_G$, and repetition of the calculation which led to eq 2.28 with a more complete form of $\langle\rho_u(\omega,T)\rangle$ must yield a self-diffusion constant with a crossover. The consequent INM-based description of strong and fragile liquids is, we think, one of the most exciting recent developments. The physically distinct contributions to $\langle\rho_u(\omega,T)\rangle$ are neatly expressed[25] in the form, suitable for fitting a broad temperature range,

$$-\ln(\langle\rho_u(\omega,T)\rangle/\omega) = a_1(T) + x_\infty(\omega) + xG(\omega,T) \tag{2.29}$$

where $x_\infty(\omega)$ determines $n_V(\omega)$ and $-xG$ is the logarithm of the averaged Boltzmann factor. In unit density LJ a very good fit for $10 > T > 0.42$ is obtained with $xG(\omega,T) = (\Omega)^{a_3(T)}$, where Ω is the scaled frequency, $\Omega = a_2\omega/T^{1/2}$ and a_2 is a constant; $a_3(T)$ goes from >4 at the glass transition to 2 at $T \gg T_{\mathrm{Fl}}$. The resulting expression for D is

$$D(T) \approx \exp-[(T_{\min}/T)^{a_3(T)/2}] \quad \text{(activated behavior only)} \tag{2.30}$$

where $T_{\min} = a_2^{\,2}\,\omega_c^{\,2}$, a microscopically motivated INM formula capable of describing strong or fragile liquids.

The parameters, and their significance, are as follows. If energy barrier fluctuations are negligible, $G(\omega,T) = \exp(-\beta\langle E(\omega)\rangle)$, and with $E \approx \omega^2$ we conclude that Arrhenius corresponds to small fluctuations. Physically, for $T \gg T_{\mathrm{Fl}}$ the potential surface is *uniformly rough* (small fluctuations) while for $T \ll T_{\mathrm{Fl}}$ it is nonuniformly rough, in accord with the ideas of Stillinger.[60] A second crossover temperature, $T_{\min}$, arises through the requirement $(T_{\min}/T) \geq 1$ for the visibility of *any* exponential T-dependence;[25,62] in our units $T_{\min} = E_{\min}$, the energy at which the available barriers begin to vanish. For $T \gg T_{\min}$, $D(T)$ is power law. Mode-coupling theory[62] predicts a crossover from power law to exponential T-dependence at a temperature T_x, but the physical pictures seem different; the viscosity diverges at T_x in early versions of mode coupling, while our crossover is not associated with a "dynamic critical point". Relaxation vs T in a supercooled liquid may be represented as a straight line in the (T_{Fl}/T), $(T_{\min}/T)$ plane, terminating at the glass transition. The plane is divided into four regions by the two crossover conditions; Figure 7 shows[25] unit density LJ, $P = 1$ atm *o*-terphenyl (OTP) and a generic strong liquid. Strength (inverse fragility) is seen to follow from a large $T_{\min}$; thus we predict that strong liquids have large ω_c. Sokolov[48] finds that a strong liquid has a relatively large contribution of harmonic vs double-well excitations. Another INM indicator of strength is then the ratio, $S = f_{\mathrm{sw}}^{\mathrm{tr}}/f_{\mathrm{dw}}^{\mathrm{tr}}$, where tr indicates translation. Nondirectional, van der Waals bonding is expected[45] to correlate with fragility, so LJ should be the ultimate fragile liquid. How can this be so for a substance with a power law $D(T)$ in almost the entire supercooled range? Figure 7 shows that LJ has an enormous range of nonuniform roughness, but a small range of exponential T-dependence due to a small $T_{\min}$. The fundamental connection is between the intermolecular interactions and the landscape, but the landscape does not manifest itself in $D(T)$ if $T > T_{\min}$.

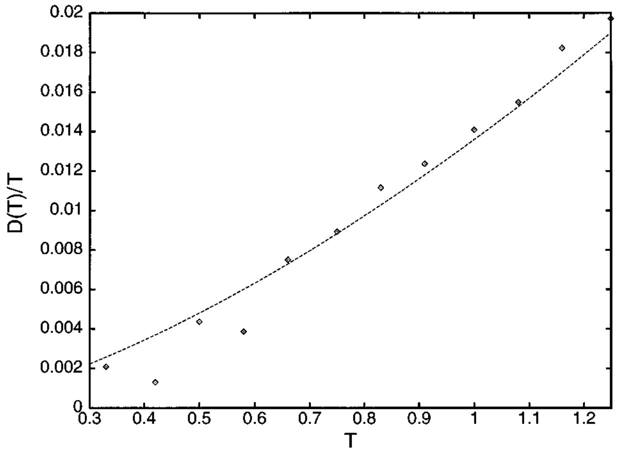

Figure 6. Prediction of eq 2.27 and simulated $D(T)/T$ (diamonds) in supercooled LJ; units for D are σ^2/τ.

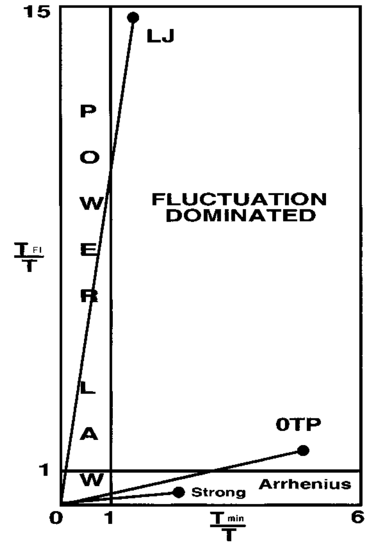

Figure 7. Schematic classification of T-dependent dynamics showing unit density LJ, normal OTP, and a generic strong liquid.

INM provides routes to the distribution of energy barriers, g(E), from $\langle\rho_u(\omega,T)\rangle$. The inverse Laplace transform of $G(\omega,T)$ with respect to β should give $g(E,\omega)$, the distribution for a given ω, but the calculation is problematic in supercooled liquids because the inverse transform of a Gaussian (eq 2.26) does not exist. The integral equations[15,16] for $g(E)$ have not yet been applied recognizing the importance of the cutoff, and it will be interesting to see how $g(E)$ behaves at low E when calculated from the DW density[20] of states. Recent discussions[63] of the breakdown of the Stokes−Einstein law just above T_G invoke fluctuations in barrier heights, associated with spatial heterogeneity, as the mechanism. If[63] the shear viscosity η depends upon the time, not the rate, for barrier crossing then

$$D\eta \approx \langle \exp(-\beta E)\rangle \langle \exp(+\beta E)\rangle \tag{2.31}$$

and the right hand side can be calculated from $g(E)$. To conclude this section, we believe that the distribution of energy barriers, organized according to imaginary frequency, is the key to both ω-dependent damping of INM correlation functions and to many properties of supercooled liquids. Analysis of $\langle \rho_u(\omega,T)\rangle$, or better, of the double-well $\langle \rho_{DW}(\omega,T)\rangle$, is the way to obtain that barrier information.

3. Summary

This article has, we hope, given an indication of the versatility and power of the INM approach to liquid state dynamics. In closing, let us consider why INM should make any sense at all; obviously, liquids are not harmonic. The theories described above, however, are not harmonic either. Even the dynamically harmonic eq 2.5 uses $\langle \rho_u(\omega,T)\rangle$ calculated from the true potential. All we ask of that zero-order description is that it hold for short times, typically a few hundred femtoseconds, and indeed it produces exact time expansions to t^4. "Short" becomes longer as T decreases, and many optical experiments explicitly focus on the femtosecond regime, but our goal is *not* to make a harmonic approximation and hope for the best. It is to use the harmonic zero-order approximation as a rich and flexible starting point for a comprehensive theory of dynamics in liquids.

The required ingredients are numerous, but at the top of the current list are the ω-dependent INM relaxation times. With these included the theory is not harmonic at all, since relaxation arises from barrier crossing, from moving out of the harmonic well. It is a great strength that the Im-ω modes yield the relaxation times. At first view, one might have thought that the presence of unstable modes would be a knotty problem, but the opposite is true. Not only can they, properly understood, make well-behaved contributions to time correlation functions, but through the averaged Boltzmann factor they provide detailed information about the potential energy landscape.

Considerable progress in the theory of simple liquids has resulted from the idea[64] that hard spheres provide a good reference system. The INM approach may be regarded as arising from a different reference system, the harmonic solid. Theories with different starting points have different strengths and weaknesses, and the strengths of the harmonic reference are at short times and in supercooled liquids. In contrast, hard spheres exhibit spurious odd terms in the time expansion of correlation functions, and the discussion of an energy landscape which has been so fruitful for supercooled liquids is impossible with a hard sphere potential.

Harmonic reference theories have a distinguished history, and it is now possible to fill in some crucial pieces missing from earlier work, such as the distribution of barrier heights, and construct a theory with true predictive power. To quote Goldstein[10] "... the theory as formulated by Eyring is an approximate one, based on certain assumptions as to the details of the motion of state points on potential energy surfaces that are as yet neither theoretically derived nor experimentally proved", and "... in whatever rigorous theory of kinetics we will someday have, processes limited by a high potential barrier will share some common simplifications of approach, and the description will not be terribly different from transition state theory." In summarizing current research in INM theory, one would not go too far wrong by saying that we have, with contemporary analytic and simulation techniques in hand, been moving in the directions indicated by the quotations.

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