Molecular Origin of Friction in Liquids

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Relaxation in liquids can often be formally attributed to "friction," a generally time-dependent quantity that can be quantitatively specified, but is difficult to break into molecular components. We show here how the instantaneous normal modes of a fluid can be used to derive this friction, thereby identifying its molecular origins. This approach is illustrated by dissecting the vibrational relaxation of a dissolved diatomic molecule into contributions from specific kinds of solvent dynamics.

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Despite the inherent many-body character of molecular liquids, frequently only a few degrees of freedom are truly of interest. Obvious examples include vibrational relaxation [1(a)], where one probes energy flow into and out of a single bond, and reaction kinetics [1(b)], where investigating chemical reactions means monitoring nothing more than a low-dimensional slice in the 10^{23}-dimensional coordinate space. The remaining degrees of freedom then act as a bath in which the special coordinates evolve.

The usual strategy for understanding such problems is to write an effective equation of motion for the tagged degree of freedom x, such as

$$m\ddot{x}(t) = \langle F \rangle - \int_0^t d\tau\, \eta(t-\tau)\dot{x}(\tau) + \mathcal{F}(t). \tag{1}$$

In such a generalized Langevin equation (GLE) [2], $\langle F \rangle$ is the force from the potential of mean force (the averaged force on x, averaging over all the bath degrees of freedom), $\mathcal{F}(t)$ describes the "random" force—the instantaneous fluctuations in the force that would be imposed by the solvent where there are no x dynamics, and $\eta(t)$ is the bath-induced friction felt by x. This time-delayed friction term occurs because of an indirect process: as x moves, the solvent responds, which in turn leads to a new force on x opposing the motion, typically a force somewhat retarded in time. What we wish to note in this Letter is that if the tagged coordinate is that of a solute dissolved in a liquid, the short-time components of the friction arise from the microscopically well-defined instantaneous normal modes [3] of the liquid.

One can always formally derive an exact GLE by projecting out the desired degrees of freedom from all the remaining degrees of freedom [2]. This derivation reveals that the friction kernel $\eta(t)$ is proportional to the autocorrelation function of the random force $\mathcal{F}$, which itself is an appropriately projected version of the actual force felt by x,

$$\eta(t) = \beta\langle \mathcal{F}(0)\mathcal{F}(t)\rangle, \qquad \beta = (k_BT)^{-1}. \tag{2}$$

Obviously, if Eq. (1) is to be regarded as a literal, rather than just a phenomenological equation of motion, one has to find a way to compute this friction kernel starting from the microscopic system Hamiltonian. It is actually possible to arrive at the exact projection by inverting molecular dynamics results [4–7], although it is much more common (and frequently quite accurate) to replace $\mathcal{F}(t)$ with the force computed while holding x fixed [7,8]. These two simulation approaches have been employed successfully for some years now in both liquid- and solid-state contexts. Still, it should be pointed out that neither procedure lends itself to any microscopic interpretation of the ingredients that make up the friction—so one does not know from what kinds of bath dynamics the friction really arises.

An intriguing finding by Zwanzig [9] was that one could represent at least the mathematics of Eq. (1) by *imagining* a microscopic Hamiltonian in which the solute coordinate was linearly coupled to a bath of harmonic oscillators x_α

$$\mathcal{H}(x,\{x_\alpha\}) = \mathcal{H}_0(x) + \sum_\alpha\left(\frac{1}{2}p_\alpha^2 + \frac{1}{2}\omega_\alpha^2x_\alpha^2\right) + \sum_\alpha c_\alpha x_\alpha x, \tag{3}$$

with $\mathcal{H}_0$ the tagged coordinate's gas-phase (isolated-molecule) Hamiltonian. For such a Hamiltonian, the exact equations of motion can be written in the form of Eq. (1) with a friction determined by the spectrum of couplings [10]

$$J(\omega) = (\pi/2)\sum_\alpha[c_\alpha^2/\omega_\alpha]\delta(\omega-\omega_\alpha). \tag{4}$$

Although the equivalence may be regarded as nothing more than a formal device, the identity has achieved a celebrity of its own in that it has become commonplace to apply GLE's by approximating or guessing a form for this spectrum of couplings [11]. The standard Ohmic form, for example, has $J(\omega)$ proportional to ω, and no time delay in friction [10]. Moreover, though there has never been any microscopic assignment of these x_α oscillators, Eq. (3) has always hinted that it might be possible to find them. That we have done so is the essential point of this paper.

Our starting point here is the observation, made rather forcefully by recent ultrafast spectroscopy experiments

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[12], that in spite of the immense range of time scales relevant to liquid dynamics (vibrational relaxation, for instance, can occur anywhere from picoseconds to tens of seconds [1(a)], one often needs to have a handle on solvent dynamics only for relatively short times in order to understand liquid-state processes. This simplification can arise either because the phenomenon itself is extremely rapid—as with solvation dynamics in simple solvents [13]—or because the crucial triggering events are short lived even if the interval between them is lengthy. Thermally activated reaction dynamics certainly falls into this latter category [14], with the short-timed solvent-influenced dynamics of a barrier crossing the crucial factor; we illustrate below that vibrational relaxation can also be thought of in this manner as well.

For subpicosecond times, then, one knows that the time evolution of liquids is frequently well described in terms of the *instantaneous normal modes* (INM's) of the liquid [3,15], the eigenvectors of the instantaneous dynamical matrix $\mathcal{D}$—the matrix of second derivatives of the potential energy evaluated at instantaneous liquid configurations. Specifically, if V_{bath} is the potential energy of an N-atom liquid with coordinates $\mathbf{R} = \{r_{j\mu}\}$ and associated mass (or moment-of-intertia) factors $m_{j\mu}$, then at any instantaneous liquid configuration $\mathbf{R}_0$

$$\mathcal{D}_{j\mu,k\nu} = \frac{1}{\sqrt{m_{j\mu}m_{k\nu}}}\left(\frac{\partial^2 V_{\mathrm{bath}}}{\partial r_{j\mu}\partial r_{k\nu}}\right)_{\mathbf{R}_0},$$
$$(j,k = 1,2,\ldots) \qquad (\mu,\nu = x,y,z,\theta,\phi,\ldots). \tag{5}$$

If $\mathcal{D}$ is diagonalized by the matrix $\boldsymbol{U}$, with eigenvalues $\omega_\alpha^2 = [\boldsymbol{U}^\dagger \cdot \mathcal{D} \cdot \boldsymbol{U}]_{\alpha\alpha}$, then it is easy to show, at least for short enough times, that the displacement of any bath coordinate in time is given by a linear combination of independent modes $q_\alpha(t) = \sum_{j\mu} \boldsymbol{U}^\dagger_{\alpha,j\mu}[r_{j\mu}(t) - r_{j\mu}(0)]$, each of which is a simple harmonic oscillator with frequency ω_α [15]. To make the connection to the single-degree-of-freedom-in-a-bath problem, suppose we simply take $V_{\mathrm{bath}}(\mathbf{R}) = V(x = x_0, \mathbf{R}) - V_0(x_0)$, where V is the total potential energy of the system, V_0 governs the x coordinate without the bath, and x_0 is an instantaneous value. The total potential energy may then be written as $V(x,\mathbf{R}) = V_0(x) + V_{\mathrm{bath}}(\mathbf{R}) + V_c(x,\mathbf{R})$, where the x coordinate-bath coupling potential V_c is defined by the difference. (One virtue of this particular decomposition is that it places the large energy scales associated with the solvation shell structure into the bath rather than relegating them to the coupling.)

With these prescriptions, an INM analysis allows us to write the Hamiltonian in precisely the form given by Eq. (3), with the modes α specifically identified as the INM's *appropriate to an instantaneous liquid configuration.* If, within the spirit of INMs, the evolution of V_{bath} and the coupling V_c are expanded through second order in displacements about the instantaneous configuration, implying that

$$V_c(x,\mathbf{R}) = V_c(x,\mathbf{R}_0) + \sum_\alpha c_\alpha q_\alpha(t)(x - x_0) + \cdots,$$

then simple linear algebra gives us molecularly explicit expressions for the liquid modes α $[x_\alpha(t) = q_\alpha(t) - f_\alpha/\omega_\alpha^2$, with f_α the instantaneous force along the αth direction], as well as spelling out the coupling coefficients for each mode,

$$c_\alpha = \sum_{j\mu} \boldsymbol{U}^\dagger_{\alpha,j\mu} m_{j\mu}^{-1/2}\left(\frac{\partial^2 V_c}{\partial x \partial r_{j\mu}}\right)_{x_0,\boldsymbol{R}_0}. \tag{6}$$

The crucial realization is that the dynamics of the tagged coordinate is well described when the Zwanzig-Hamiltonian-derived friction is specified with just these instantaneous ingredients and then averaged over liquid configurations [16],

$$\begin{aligned}\eta(t) &= \left\langle \sum_\alpha \frac{c_\alpha^2}{\omega_\alpha^2}[\cos\omega_\alpha t - 1]\right\rangle \\ &= \int_0^\infty d\omega\, \rho_{\mathrm{fric}}(\omega)[\cos\omega t - 1]/\omega^2,\end{aligned} \tag{7}$$

thereby assigning the spectrum of couplings of Eq. (4) as $J(\omega) = (\pi/2)\omega^{-1}\rho_{\mathrm{fric}}(\omega)$ [10], with the "friction spectrum" $\rho_{\mathrm{fric}}(\omega) = \langle \sum_\alpha c_\alpha^2 \delta(\omega - \omega_\alpha)\rangle$, nothing more than a weighted INM density of states.

A number of comments are in order at this point. These results are actually deceptive in their apparent simplicity. It is true that our basic approach relies on nothing more than how dynamical quantities evolve at short times; in particular, since we average over the fully anharmonic distribution of instantaneous starting points, we are *not* simply assuming harmonic behavior. There are a number of nontrivial consequences of this approach, however. For one thing, the instantaneous configuration-to-configuration fluctuations of our friction will be significant, as with any local density of states. It thus needs to be verified that averaged solute dynamics can be written in terms of just the averaged friction. Moreover, the friction as defined by Eq. (7) is, in fact, the instantaneous *change* in the friction [what would correspond to $\eta(t) - \eta(0)$ in other treatments]. As a result, our $\eta(t = 0) = 0$ and the second fluctuation-dissipation theorem, Eq. (2), holds only in the rather unusual second-derivative form

$$\ddot{\eta}(t) = -\beta\langle \dot{\mathcal{F}}(0)\dot{\mathcal{F}}(t)\rangle.$$

We might also note that because of the non-Debye-like character of the INM density of states, the power spectrum of our friction actually diverges as $\omega \to 0$, a result not inconsistent with the inappropriateness of INM developments at long times [17].

Despite this litany of potential pitfalls, these results turn out to be of considerable utility in understanding liquid-state relaxation. An obvious benefit of this formulation is that it enables us to derive and interpret the friction starting from the intermolecular potentials, without us having to evaluate the full many-body dynamics first. As a

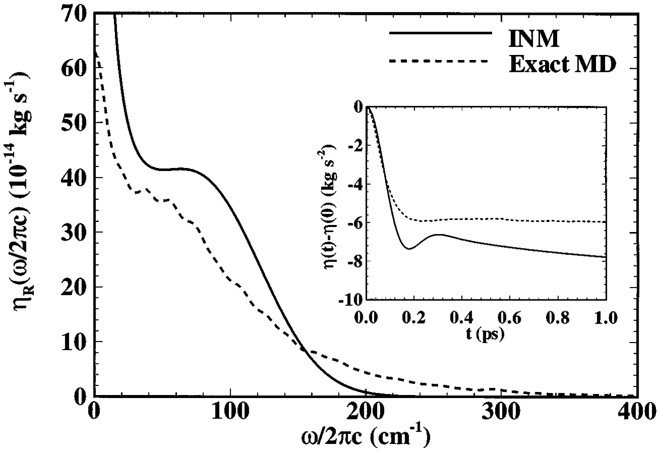

FIG. 1. The real part of the frequency-domain friction (main panel) along with the time-domain friction (inset) seen by a nonrotating diatomic dissolved in a supercritical atomic liquid. The solid curves are the INM prediction, whereas the dashed curves are the Berne *et al.* results from the full dynamics for a flexible diatomic with an isolated frequency of $\omega_0 \approx 150$ cm^{-1} [7]. Numerical results are presented in this figure and subsequently assume an Ar solvent [20].

concrete example, consider, as several authors have done recently, the vibrational population relaxation of a solvated diatomic molecule [6,7,17–19]. The comparison of the friction derived from the complete dynamics [7] with that computed from the INM's, Fig. 1, makes it evident that the essence of the friction is indeed captured by the liquid's INM's [20]. Somewhat more quantitatively, a comparison of Landau-Teller [18] predictions for the vibrational energy relaxation rates T_1^{-1} between INM and molecular dynamics [6] calculations of the friction (Table I) indicates that this analysis allows us to gain insight into dynamics significantly slower than the few hundred fs one normally thinks of as defining the limits of validity of INM's [3].

TABLE I. Vibrational energy relaxation rates. The Landau-Teller prediction for this relaxation rate is $1/T_1 = \mu^{-1}\eta_R(\underline{\omega})$, with μ the reduced mass of the solute, η_R the real part of the (frequency-domain) friction, and $\underline{\omega}$ the renormalized solute frequency. The model used here simulates a diatomic dissolved in Ar; further details are given in Ref. [20].

$\omega_0/2\pi c$ (cm^{-1})	$\underline{\omega}/2\pi c$ (cm^{-1})	$1/T_1$ − INM (ps^{-1})[a]	$1/T_1$ − MD (ps^{-1})[b]
49.5	39.7	12.69	11.26
74.3	68.7	12.50	9.64
148.6	145.0	3.26	3.16
222.8	221.6	0.05	0.99

[a] Instantaneous-normal-mode prediction (this work).
[b] Prediction based on numerically exact friction derived from full molecular dynamics [7].

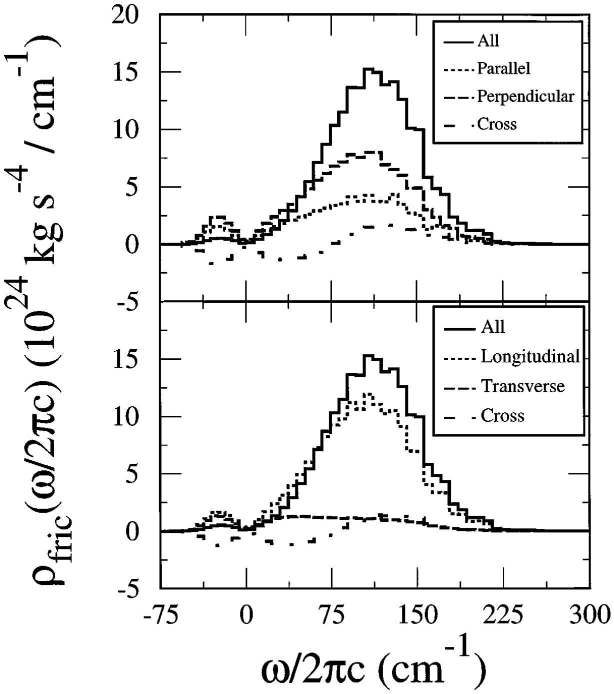

FIG. 2. Parallel (perpendicular) [upper panel, (a)] and longitudinal (transverse) [lower panel, (b)] projections of the INM friction spectrum. Following the usual convention, the imaginary modes are plotted on the negative frequency axis.

This ability to specify the friction molecularly has a number of interesting implications. We can, for example, use Eqs. (6) and (7) to discover which portions of the friction arise from which kinds of molecular motion. If we resolve $\rho_{\rm fric}(\omega)$ into components [21] derived from solvent motion parallel and perpendicular to the vibrating bond in our example, Fig. 2(a), we find that the two kinds of dynamics are statistically indistinguishable: They contribute 34.2% and 65.8% of the friction (a 1:2 ratio), respectively. However, when we look at motion longitudinal and transverse with respect to the line connecting the center of mass of the diatomic with each solvent atom, Fig. 2(b), we discover that the friction is clearly dominated (85.5%) by longitudinal solvent motion. More generally, the fact that we can phrase vibrational relaxation phenomena in terms of the INM's of the solvent suggests that the recent conjecture by Moore *et al.* [19] that liquid INM's should resemble solid-state phonons in their role as discrete energy absorbing excitations is actually correct. Despite their remarkably short individual lifetimes, the ability of a set of INM's to generate a friction means that the resulting GLE will produce phenomenology mimicking that of genuine, stable, oscillatory degrees of freedom. What we now may have is the possibility of understanding the real liquid motions behind this facade.

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[16] The evidence we present here is purely numerical, but as we shall show in a subsequent paper, this prescription does guarantee exact short-time behavior.

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[19] The idea that vibrational relaxation in liquids should be amenable to some kind of normal-mode analysis is not entirely new. Beside the pioneering work of Schvaneveldt and Loring [17], P. Moore, A. Tokmakoff, T. Keyes, and M.D. Fayer, J. Chem. Phys. **103**, 3325 (1995), have speculated that the INM density of states should act as a solid-state phonon band. In addition, in work published after this paper was submitted, J. Cao and G.A. Voth, J. Chem. Phys. **103**, 4211 (1995), have recently shown that their semiempirical optimized normal modes can be used to compute bond friction to high accuracy.

[20] Following Ref. [7], all calculations reported here used nonrotating diatomic solutes (with isolated-molecule frequencies ω_0 and equilibrium bond length x_{eq}) dissolved in atomic liquids composed of atoms identical to those in the solute—all governed by Lennard-Jones intermolecular interactions (with standard parameters ε and σ) at the same point ($\rho\sigma^3 = 1.05, k_B T/\varepsilon = 2.5$). The INM friction spectrum itself, $\rho_{\mathrm{fric}}(\omega)$, results from 10^4 108-particle molecular dynamics (MD) snapshots, each separated by $0.05\tau_{\mathrm{LJ}}$ [$\tau_{\mathrm{LJ}} = (m\sigma^2/\varepsilon)^{1/2} \sim 2$ ps for liquid argon: mass $m = 40$ amu, $\varepsilon = 120$ K, and $\sigma = 3.41$ Å], with the solute held rigid at $x_{\mathrm{eq}} = 1.25\sigma$ and spatially fixed. Note that only configurational information, not dynamics, is used in these INM calculations.

[21] The projection operator $\boldsymbol{P}^{\mathbf{A}} = \boldsymbol{U}^\dagger \hat{\mathbf{A}}\hat{\mathbf{A}}^\dagger \boldsymbol{U}$ and its complement $\boldsymbol{P}^{\perp\mathbf{A}} = \boldsymbol{U}^\dagger(\mathbf{1} - \hat{\mathbf{A}}\hat{\mathbf{A}}^\dagger)\boldsymbol{U}$, with $\mathbf{1}$ the unit matrix, are the operators required to project out the contribution along (and orthogonal to) the unit vector $\hat{\mathbf{A}}$. For a more detailed description of the INM projection, see Ref. [15].