The Instantaneous Normal Modes of Liquids

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I. Liquids Are Not Held Together by Springs

It hardly needs saying that the presence, and indeed the dynamics, of liquids plays a crucial role in chemical processes ranging from electron transfer[1] to acid–base chemistry.[2] Sometimes this role is merely the result of the solvent's availability as a reactant present in huge excess, but more generically, it arises becauses solvents can *solvate*: they can alter the energy of a species in striking fashion.[3] The classic freshman textbook example points out that it would be energetically unlikely for Na to ionize in water (the octet rule notwithstanding) were it not for the solvation afforded the resulting Na^+ ions.[4] Suppose, then, that one wanted to understand this solvation process in some detail. There is presumably a significant free energy barrier that must be overcome in order for water to rearrange itself so as to accommodate a solute, so how, *precisely*, will water molecules reorient and translate so as to provide the optimum compromise between their own eminently satisfactory hydrogen-bonding network and the annoying demands of an interloper solute molecule? How fast will they adopt the preferred geometry? Which particular motions will happen first?

Unfortunately, it would not take all that pessimistic an outlook to predict that we will never be able to understand the motion of molecules in liquids in

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sufficient detail to be able to tackle these questions. The behavior of molecules in gases is easy; the average intermolecular distances are so large that molecules can be regarded as all but solitary creatures whose tranquil existence is disturbed only infrequently and only then by the presence of a single intruder at a time. Solids might seem a much more difficult case, but they too often turn out not to present all that much of a challenge. As long as we restrict ourselves to small oscillations about perfect crystalline order, it is possible to regard the motion of a single molecule in a solid as being just a small part of one of the various possible simultaneous (collective) motions of the entire crystal. These collective motions—the phonons of the crystal—are as independent from one another as individual molecules are in a gas, and they are consequently just as simple to handle. But what of liquids?

Liquids being almost as dense as solids (and occasionally even more dense), there is not overmuch temptation to pretend that liquids are gases, but the hope that they can be thought of as solids resurfaces over and over again in the literature. The fervent wish that some sort of phonon description might capture the essence of the dynamics has proven just too seductive to abandon. The immediate reaction to this idea, though, with more than a little justification, is that it is not all that sensible. Phonon pictures require that the intermolecular forces can be regarded as harmonic, and liquids can simply not be viewed as being held together by springs. The success enjoyed by modern theories of liquid structure is, in fact, based on the notion that the intermolecular forces that determine equilibrium molecular arrangements are

often so sharply varying and strongly repulsive that liquids can frequently be thought of as a case study in randomly packing hard objects.[5] Moreover, the standard justification for a harmonic picture working in solids is that the atoms are merely executing small oscillations about some stable structure. Since the arrangement is stable, the first derivative of the potential energy must vanish. So, to first order, there is no effect of an atomic displacement; the first nonvanishing contribution must therefore be quadratic in the displacements, making the potential purely harmonic for suitably tiny displacements. In liquids, on the other hand, any instantaneous snapshot would reveal a structure that was *not* mechanically stable. Nor, for that matter would one expect displacements to be small. Atoms in liquids will diffuse and the liquid as a whole will flow.

This gloomy picture having been painted for our prospects for understanding the dynamics of liquids, it might come as somewhat of a surprise to learn how promising the outlook really is. An intriguing confluence of theoretical and experimental developments have recently shown how one can actually begin to answer microscopically detailed questions about processes such as solvation.[6] New theoretical developments in the study of liquid excitations, in particular,[7-15] have pointed the way to accurate descriptions of liquid-state molecular motions that are, of all things, harmonic. As we shall describe in the remainder of this Account, one of the main characteristics of such newer harmonic approaches (*instantaneous-normal-mode* theories) is that they are deliberately designed to work well at short times. This feature is an especially intriguing one in that it focuses our attention on precisely the kinds of time intervals that recent ultrafast spectroscopic experiments have shown to be crucial to solvation.[16,17]

II. What Instantaneous Normal Modes Are and Are Not

The difficulties with harmonic interpretations of liquid motion notwithstanding, there is a rather long history of both harmonic pictures and harmonic methods being applied to liquids, often with reasonable success. Some of these applications are of the "it sure looks like an oscillator" variety: there is no direct identification of what is supposed to be oscillating (because all that is observed is some sort of averaged, collective, response), but various properties of the liquid do seem to resemble what would be seen if there were some kind of coherent oscillation occurring. Historically, the most important examples in this category are instances in which one interprets peaks in the inelastic neutron scattering data (that is, the spectrum of density fluctuations as measured by the inelastic structure factor of the liquid $S(k,\omega)$) as if they represented identifiable motions. Within such a framework, one can distinguish liquids such as molten salts and liquid metals from liquids such as Ar by the extent to which they have "propagating modes", and one even talks about the wave vectors, polarizations, and speeds of propagation of the modes.[18]

At the opposite extreme are the "it doesn't matter if the oscillators are there or not" cases. In these examples, one takes advantage of the marvelous mathematical properties of a collection of harmonic oscillators to create a formal representation of some piece of macroscopic phenomenology. The classic instances here involve the description of a variety of solute properties with generalized Langevin equations.[19] Ever since Zwanzig pointed out that it is possible to think of both friction and the random forces as if they came from a set of simple harmonic oscillators instead of from a real solvent,[20] generalized Langevin equations have found themselves in the midst of problems ranging from chemical reaction kinetics[21] to vibrational relaxation.[22] What has made them increasingly popular in recent years is the fact that there is a more or less well-defined route from computer-simulatable correlation functions (such as the force or the velocity autocorrelation functions) to what is often referred to as the spectral density of the hypothetical harmonic bath.[23] There is no presumption that such harmonic oscillators are in any sense real, and there are technical issues relating to the fact that the correlation functions one needs as input ought to be "projected" rather than ordinary correlation functions,[24] but the lure of replacing a solvent by a set of springs has proven remarkably difficult to resist. Much the same might be said of the Brownian oscillator description of spectroscopic behavior in solution.[25] Here one simply postulates the existence of a set of damped oscillators in order to mimic the experimental observations that spectra in solution exhibit dephasing and energy relaxation. Unfortunately, there has been no analog proposed for the Zwanzig theorem that underlies the generalized Lan-

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gevin equations, but the ability of Brownian oscillators to represent the data is often welcome.

Motivated in part by such harmonic bath applications, there have been a number of first principles theoretical attempts at prescribing what the phonons in a liquid ought to be. Two of the more promising studies were by Hubbard and Beeby[26] and by Zwanzig.[27] Both of these attempted to arrive at a single number for the phonon frequency (or the frequency as a function of wave vector) by looking at liquids on the average, the former by looking at the approximate linear response to a periodic probe, and the latter by estimating the eigenvalues of the Liouville operator. Because of the averaging, however, one always lost the microscopic identity of the phonon mode, meaning that there was no way to associate a mode with the particular movements of particular atoms. An intriguing alternative which does not suffer from this problem is provided by the quenched normal modes associated with the Stillinger–Weber inherent structures of liquids.[28] The idea here is to quench the liquid repeatedly to find the minima on the liquid's potential energy surface and once there perform a standard small-oscillation normal-mode analysis.[29] So far, though, there has been no analytical theory showing how one might understand the resulting spectra, so the procedure has functioned largely as a computer simulation algorithm, albeit a rather conceptually useful one.

The instantaneous normal modes,[9,30-41] for better or worse, differ in significant ways from all of these approaches. It should be emphasized that the computational scheme for generating them has been applied from time to time for almost 20 years,[42-44] but what seem to be the new features are, first, the realization that instantaneous normal modes can provide an accurate picture of the short-time dynamics of liquids at a completely microscopic level and, second, that, despite their wealth of detail, one can actually understand some of their properties from the statistical mechanics of liquids.

The "modern" derivation of the concept proceeds as follows:[9,30,31] Suppose we ask how the potential energy V of a liquid differs at some time t from what it was at time 0. What difference there is arises from the change in the liquid configuration ($\mathbf{R}_t - \mathbf{R}_0$), so *if the time interval is short enough*, we can expand the potential energy difference in powers of this change,

$$V(\mathbf{R}_t) \approx V(\mathbf{R}_0) - \mathbf{F}{\cdot}(\mathbf{R}_t - \mathbf{R}_0) + $$
$$\tfrac{1}{2}(\mathbf{R}_t - \mathbf{R}_0){\cdot}\boldsymbol{D}{\cdot}(\mathbf{R}_t - \mathbf{R}_0) \quad (1)$$

where $\mathbf{F}$ is the instantaneous (time 0) force and $\boldsymbol{D}$, the dynamical matrix, is the instantaneous Hessian matrix of second derivatives of the potential energy.[45] Every new liquid configuration (that is, every new choice of time 0) will have its own force and dynamical matrix, but for each choice there is a variable transformation—a matrix U—that will diagonalize $\boldsymbol{D}$, turning the $3N$ Cartesian coordinates of the N atoms into $3N$ collective coordinates $\mathbf{q}(t) = (q_\alpha(t); \alpha = 1, ..., 3N)$ and our expression for the potential energy difference into a sum of independent harmonic contributions:

$$\mathbf{q}(t) = \boldsymbol{U}{\cdot}(\mathbf{R}_t - \mathbf{R}_0) \quad (2)$$

$$V(\mathbf{R}_t) = V(\mathbf{R}_0) + \sum_\alpha \{ -f_\alpha q_\alpha(t) + \tfrac{1}{2}\omega_\alpha^2 q_\alpha^2(t) \} \quad (3)$$

Here, the quantities f_α and ω_α^2 are the components of the transformed force and the eigenvalues of the dynamical matrix, respectively.

$$f_\alpha = [\boldsymbol{U}{\cdot}\mathbf{F}]_\alpha$$

$$\omega_\alpha^2 = [\boldsymbol{U}{\cdot}\boldsymbol{D}{\cdot}\boldsymbol{U}^T]_{\alpha\alpha}$$

What one might call the instantaneous-normal-mode perspective, then, is that the dynamics of a liquid at short times is governed by precisely the dynamics of these $q_\alpha(t)$ modes

$$\mathbf{R}_t = \mathbf{R}_0 + \boldsymbol{U}^T{\cdot}\mathbf{q}(t) \quad (4)$$

and that this dynamics, in turn, is nothing but simple harmonic motion for the coordinates q_α and the corresponding velocities v_α:

$$q_\alpha(t) = (f_\alpha/\omega_\alpha^2)(1 - \cos \omega_\alpha t) + [v_\alpha(0)/\omega_\alpha](\sin \omega_\alpha t)$$

$$v_\alpha(t) = v_\alpha(0) \cos \omega_\alpha t + (f_\alpha/\omega_\alpha^2)(\sin \omega_\alpha t) \quad (5)$$

In this treatment the time evolution of a liquid configuration is completely prescribed by the set of instantaneous forces f_α, frequencies ω_α, and velocities $v_\alpha(0)$. Thus, in practice, all that one needs to know are the probability distributions of these equilibrium quantities (as determined by the equilibrium distribution of liquid configurations) in order to be able to compute the short-time behavior of any desired time correlation function. Moreover, the fact that the

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answers so derived will usually end up being a sum of contributions from each mode α will give us a nice physical interpretation. We will be able to think of the dynamics as if it arose from a variety of collective, but mutually independent, harmonic modes.

It is probably worth making the point fairly strongly that this approach is really quite narrow in its claims as to what is and is not harmonic in a liquid. To begin with, because the instantaneous frequencies and forces vary from liquid configuration to liquid configuration, the formalism does not imply that any of the liquid's statistics are necessarily Gaussianly distributed. In fact, there is neither an expectation nor a necessity that any *equilibrium* properties will be governed by harmonic potentials; the theory has nothing to say about the values of purely thermodynamic quantities such as heat capacities.[46] By way of contrast, most other harmonic treatments of liquids, quite sensibly, make no such distinctions between the potentials governing static and dynamic properties. Indeed instantaneous-normal-mode theories are somewhat internally inconsistent in this regard: they are compelled at very long times to yield the distribution of liquid configurations that one would obtain if the intermolecular interactions were governed by harmonic forces instead of the true forces, in violation of the fluctuation dissipation theorem. Provided that one is interested in times well short of this asymptotic behavior, however, we are actually guaranteed to have a sensible prescription—derivable from the true intermolecular potentials—for casting the dynamics of liquids into harmonic terms. The reasonableness of this approach is evidenced, among other things, by theorems assuring us of the accuracy of our predicted dynamics. Both velocity autocorrelation functions and solvation correlation functions, for example, are guaranteed to be correct through order t^4.[31,34]

III. Applications of Instantaneous Normal Modes

The instantaneous-normal-mode concept has now been successfully applied to a surprisingly wide range of problems, many of which have little to do, in a direct sense, with short-time dynamics. The more notable instances involve calculating diffusion constants,[30,36] handling multiple time scales,[47] investigating the nature of glasses,[48] and mapping the topography of the potential surfaces of anything from colloids to proteins.[33,37,48,49] Partly because of space limitations, but also to highlight the rather different perspective just outlined, we shall not be discussing any of these studies here. Instead we shall just present a few applications which specifically illustrate the power of the approach in illuminating the "transient" dynamics that seems to govern so much of liquid behavior.

A. The Instantaneous-Normal-Mode Spectrum Itself. In most applications, the distribution of instantaneous-normal-mode frequencies would be com-
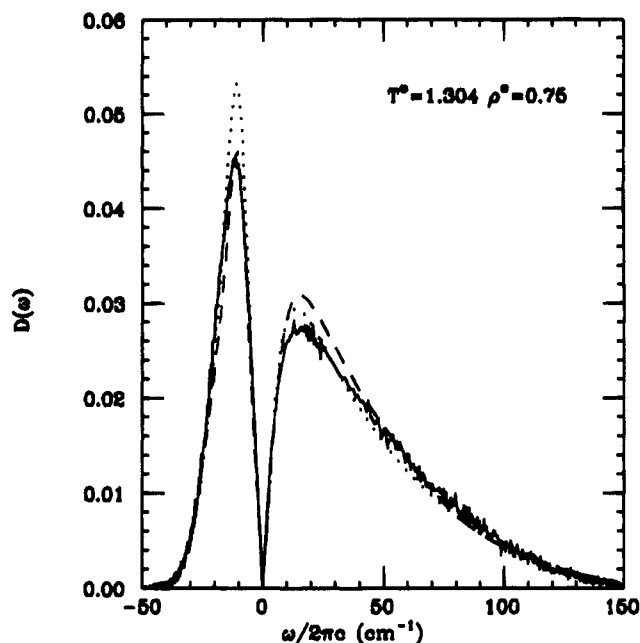

Figure 1. Instantaneous-normal-mode spectrum of liquid Ar at 158 K and at a density of 1.27 g/cm³ as computed by simulation (solid line) and by two different levels of analytical theory (dashed and dotted lines).

puted simply by generating an equilibrium ensemble of liquid configurations via simulation, constructing the dynamical matrix for each configuration, and then performing numerical diagonalizations. However, for atomic liquids, as illustrated in Figure 1, the distribution of eigenvalues of this sort can be mapped into more conventional liquid problems, enabling us to bring the analytical techniques of liquid theory to bear and providing us with some insight into the physical origins of the various features.[32] Indeed, the spectrum shown in Figure 1, that of a rare gas liquid, is not all that atypical of the spectra one would obtain for most liquids, including both polar[33,35] and nonpolar[31,38,50] molecular liquids, and atomic mixtures.[41] There is a signature right-triangle shape to the positive-eigenvalue portion of the spectrum, which arises from the prevalence of the soft (low-frequency) motions that are possible in any liquid, and there is a small, but not insignificant, fraction of imaginary modes (i.e., those for which the eigenvalues $\omega^2 < 0$), which are depicted, for convenience, on the negative frequency axis. These, too, are a universal feature of liquids (though they are also seen in hot solids) since they reflect the presence of negative curvatures on the potential surface, without which it would be impossible to have the barriers and saddle points that must be present in a mechanically unstable substance.

These special characteristics of liquid spectra have actually been used as a marker for phase changes in small clusters.[30,44] As is apparent in Figure 2, even an Ar₁₃ cluster will exhibit a liquid-like spectrum at sufficiently elevated temperatures. By way of contrast, the disappearance of the imaginary modes, the loss of the right-triangle shape, and the feature at 60 cm⁻¹ (which is precisely the location of the longitudinal mode peak in the bulk solid's phonon spectrum)[51]

(46) See, however, ref 37 for attempts to make use of instantaneous normal modes to ascertain equilibrium quantities.

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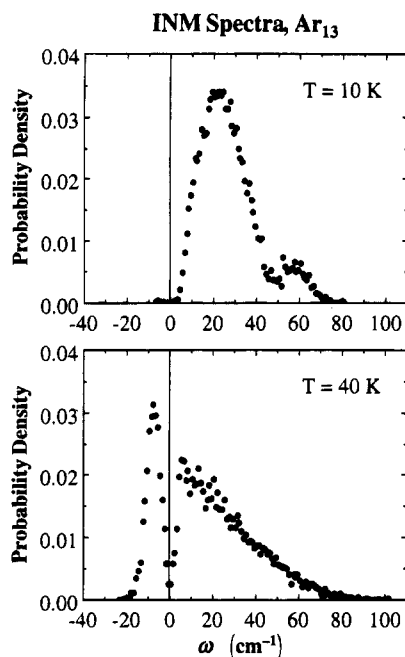
Figure 2. Instantaneous-normal-mode spectrum of an Ar_{13} cluster under solid-like conditions (upper panel) and liquid-like conditions (lower panel).
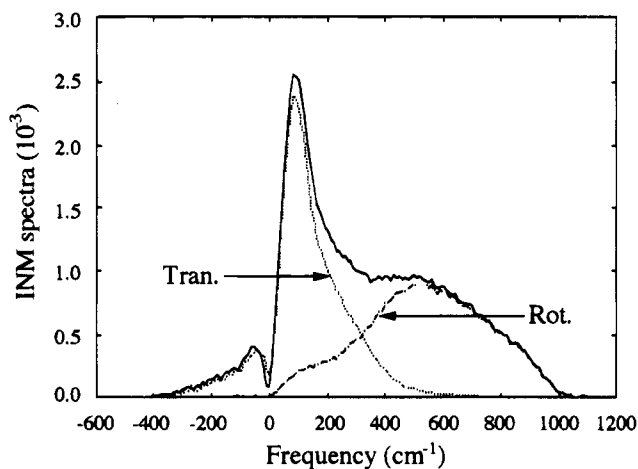

Figure 3. Instantaneous-normal-mode spectrum of liquid H_2O under ambient conditions (298 K and 1 g/cm³). Also shown here are the translational and rotational components of the spectrum (as determined by the instantaneous-normal-mode eigenvectors).

all suggest that the low-temperature form is quite solid-like. While there is no sudden transition between these two kinds of spectra, the mere existence of two such different kinds of dynamics has helped to clarify what it means to speak of distinct phases in a cluster.

Lest the impression be given that Ar is all there is to liquids, it should be noted that not every liquid's spectrum has an identical appearance. If one examines the spectrum of liquid H_2O (Figure 3),[33] one is struck by the relatively small fraction of imaginary modes (only 6% of the total, as opposed to 21% in liquid CH_3CN and as many as 33% in liquid Ar)[32,35] and by the distinctive high-frequency peak. Significantly, because the modes themselves are known in microscopic detail, we can easily establish the origin of this peak. By projecting out the proportions of each mode that correspond to rotational and translational degrees of freedom (Figure 3),[31,33] we see that the high-
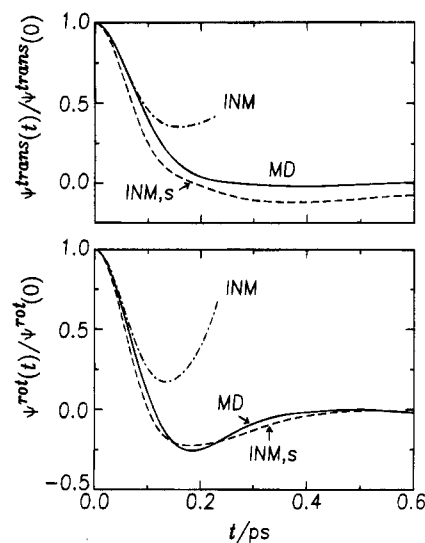

Figure 4. Normalized translational (upper panel) and rotational (lower panel) velocity autocorrelation functions for neat liquid CH_3CN under ambient conditions (293 K, 1 atm). In both cases, the solid line is the exact molecular dynamics result, the dot-dashed line is the full instantaneous-normal-mode prediction, and the dashed line is the instantaneous-normal-mode prediction obtained when only real (stable) modes are included.

frequency motion is almost entirely due to molecular libration, hardly surprising in a strongly hydrogen bonding fluid. What is perhaps a bit more surprising is that the spectrum of center-of-mass translations still strongly resembles that of nonassociated fluids, despite the presence of these same hydrogen bonds. In fact, what one invariably sees is that the instantaneous-normal-mode spectra of liquids differ from one another mainly in their rotational portions; the dynamics of net molecular translation seems to be fairly universal.[52]

B. Predictions for Dynamics. Equations 4 and 5 tell us, in principle, everything we need to know to understand liquid dynamics. For example, simply by using eq 5 and averaging over the equilibrium quantities, it is straightforward to show that the (single-molecule) translational-velocity and angular-velocity autocorrelation functions are simply Fourier transforms of $D^{trans}(\omega)$ and $D^{rot}(\omega)$, the translational and rotational portions of the liquid's spectrum:[31]

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle / \langle \mathbf{v} \cdot \mathbf{v} \rangle = \int d\omega \, D^{trans}(\omega) \cos \omega t$$

$$\langle \bar{\omega}(0) \cdot \bar{\omega}(t) \rangle / \langle \bar{\omega} \cdot \bar{\omega} \rangle = \int d\omega \, D^{rot}(\omega) \cos \omega t \qquad (6)$$

As we see for CH_3CN (Figure 4)[35] and for H_2O (Figure 5),[33] the predictions can be quite remarkable at short times. Physically, these functions convey the extent to which a molecule in a liquid remembers its center-of-mass or angular momentum, so where these functions are most negative is the time at which the velocity is most out of phase with the initial velocity, which, in some sense, reflects the extent of the molecular "rebound" from its surrounding solvent cage. Though it is a highly intuitive concept, the

(52) If one removes the restriction to rigid molecular models, the instantaneous normal modes of a molecular liquid will also include contributions from intramolecular vibrations.[38] These (largely) intramolecular modes will, of course, differ greatly from liquid to liquid.
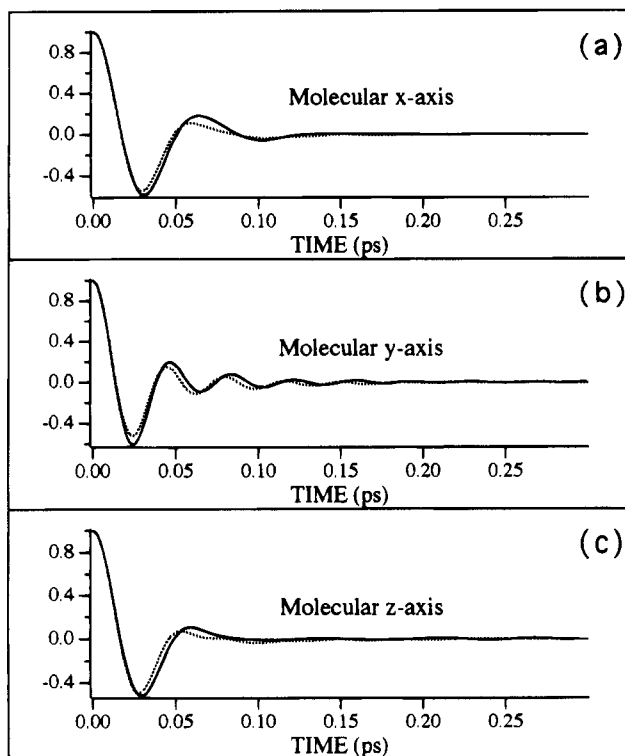
Figure 5. Normalized angular-velocity autocorrelation functions for neat liquid H_2O relative to the three principal molecular axes. The solid line is the exact molecular dynamics result, and the dotted line, the instantaneous normal-mode prediction (neglecting imaginary modes).

Figure 6. Solvation spectrum of acetonitrile (as seen by a dipolar solute), along with the projections into rotational, translational, and rotation–translation-coupled parts.

strongly collective character of cage-like behavior makes it difficult to capture from first-principles theories.[53] The ability of this approach to encompass the cage idea, and to do so within a simple harmonic model, is therefore particularly welcome.

It should be pointed out (in the interest of truth in advertising) that in performing these calculations one has to discard the imaginary modes from the spectra in order to prevent unphysical divergences of the correlation functions.[31] This procedure does make a certain amount of physical sense in that the imaginary modes are indicative of motion that is, in a literal (Lyapunov) sense, unstable.[54] Simply put, the places where the local potential curvature is negative are terrible locations from which to extrapolate future dynamics. Nonetheless, having to ignore any of the spectrum is a bit disconcerting.[55] Fortunately for our present purposes, the fraction of imaginary modes is relatively small in interesting solvents and the fraction of such modes that contribute to short-time solvation dynamics turns out to be even smaller.[33,35] Still, it remains an interesting open question whether what these modes are really trying to tell us is information about the long-time dynamics.[37]

Our final, and most revealing, illustration of instantaneous normal modes takes us back to the question we posed at the beginning of this Account: How, precisely, does solvation take place? The kinds of

correlation functions of interest now are those that look at the fluctuations δA in the solute–solvent interaction A,

$$C(t) = \langle \delta A(0) \ \delta A(t) \rangle / \langle (\delta A)^2 \rangle$$

since the rate at which the solvent accomplishes the solvation process is proportional (at least in linear response theory) to just these functions.[56] To evaluate this correlation function we can look at an intimately related, and somewhat easier to calculate, function, the solvation velocity correlation function:

$$G(t) = \langle \dot{A}(0) \ \dot{A}(t) \rangle = -\langle (\delta A)^2 \rangle \ (d^2 C(t)/dt^2)$$

If we assume, within the spirit of the instantaneous-normal-mode idea, that the time interval which the interaction $A(t)$ evolves is small, then we can expand in powers of the instantaneous normal modes:

$$A(t) = A(0) + \sum_\alpha A'_\alpha q_\alpha(t) + \ldots$$

$$A'_\alpha = (\partial A/\partial q_\alpha)_{t=0}$$

We can truncate this expansion at any order we have the patience for, but within a linear theory, substituting eq 5 yields the amazingly simple result that $G(t)$ is just the Fourier transform of what one might call the *solvation spectrum*, $\varrho_{solv}(\omega)$,

$$G(t) = k_B T \int d\omega \ \varrho_{solv}(\omega) \cos \omega t \qquad (7)$$

$$\varrho_{solv}(\omega) = \langle \sum_\alpha (A'_\alpha)^2 \delta(\omega - \omega_\alpha) \rangle \qquad (8)$$

which is nothing more than the distribution of mode frequencies weighted by how efficiently each mode couples to the solute.[34]

The solvation spectrum itself is an interesting object, as we can see from the case of liquid CH_3CN (Figure 6).[35] The fact that the bulk of this spectrum

(53) Lynden-Bell, R. M.; Steele, W. A. *J. Phys. Chem.* **1984**, *88*, 6514. Lynden-Bell, R. M.; Hutchinson, D. J. C.; Doyle, M. *J. Mol. Phys.* **1986**, *58*, 307. Ruhman, S.; Nelson, K. A. *J. Chem. Phys.* **1991**, *94*, 859. Patron, F.; Adelman, S. A. *Chem. Phys.* **1991**, *152*, 121.

(54) Eckmann, J.-P.; Wayne, C. E. *J. Stat. Phys.* **1988**, *50*, 853.

(55) For example, the exact theorems that predict that instantaneous normal mode formulas are accurate to order t^4 rely on *all* of the modes being included in the calculation, including the imaginary ones.
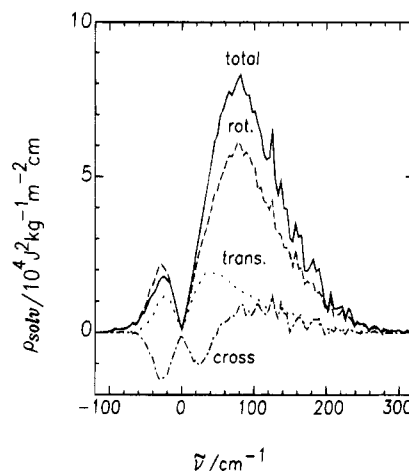
(56) Maroncelli, M.; Fleming, G. *J. Chem. Phys.* **1988**, *89*, 5044. Bader, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501.

(57) The first-shell response is generated by extending the rotational/translational projection analysis mentioned in the text so as to discriminate by distance scales as well. For this example, the relaxation of the solvent as a whole is actually noticeably slower than that of the first shell alone and is less well described by linear solvation theory beyond the first 200 fs.
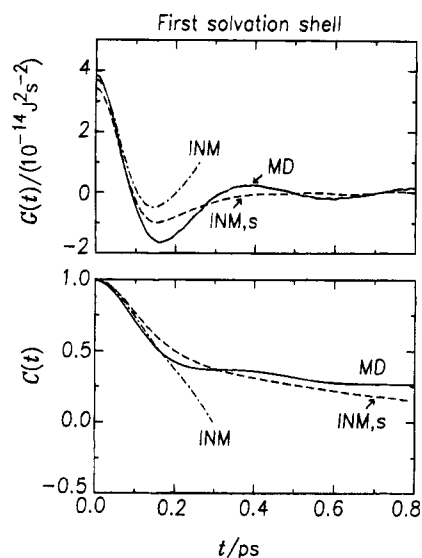
Figure 7. Contributions to the solvation time correlation functions from the first solvation shell for a dipolar solute dissolved in liquid acetonitrile.[57] For both the experimentally relevant $C(t)$ correlation function and the related $G(t)$ correlation function (defined in the text), the solid line is the exact molecular dynamics result, the dot-dashed line is the full instantaneous-normal-mode prediction, and the dashed line is the instantaneous-normal-mode prediction obtained when only real (stable) modes are included.

belongs to rotational motion tells us that the overwhelmingly majority of early solvation events in polar solvation arise from solvent reorientation. Somewhat more quantitatively, since one can show rigorously that the solvation frequency ω_{solv}, defined by fitting $C(t)$ at early times to a Gaussian decay

$$C(t) \approx \exp\left[-\frac{1}{2}(\omega_{solv}t)^2\right]$$

scales with the area under the solvation spectrum

$$\omega_{solv}^2 = (k_BT/\langle(\delta A)^2\rangle)\int d\omega \, \varrho_{solv}(\omega) \qquad (9)$$

it is clear that some 76% of the initial solvation in this case is librational in character. The ultrarapid initial decay of the actual solvation correlation functions (Figure 7) can therefore easily be analyzed in molecular terms.[35,50]

IV. Concluding Remarks

Perhaps the real power of the kinds of analysis discussed here will not so much lie in providing yet another set of vibrational frequencies that one can associate with liquids as it will reside in the molecular definitions of the modes themselves. The intriguing idea that each mode describes a genuinely collective many-body motion operating in a liquid may ultimately prove to have more far reaching consequences than any aggregate spectrum. Of course, these modes are derived from a purely harmonic treatment and we certainly do not expect to be able to ignore forever the hard fact that liquids are anharmonic. Even so, it may be worth remembering that the need to incorporate anharmonicity has hardly lessened the conceptual and computational value of traditional normal modes as useful points of departure for numerous more sophisticated approaches to small-molecule dynamics. Perhaps our understanding of the dynamics of liquids will eventually follow a similar path.