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Extensions to the instantaneous normal mode analysis of cluster dynamics: Diffusion constants and the role of rotations in clusters

John E. Adams

Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211

Richard M. Stratt

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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For the instantaneous normal mode analysis method to be generally useful in studying the dynamics of clusters of arbitrary size, it ought to yield values of atomic self-diffusion constants which agree with those derived directly from molecular dynamics calculations. The present study proposes that such agreement indeed can be obtained if a sufficiently sophisticated formalism for computing the diffusion constant is adopted, such as the one suggested by Madan, Keyes, and Seeley [J. Chem. Phys. **92**, 7565 (1990)]. In order to implement this particular formalism, however, we have found it necessary to pay particular attention to the removal from the computed spectra of spurious rotational contributions. The utility of the formalism is demonstrated via a study of small argon clusters, for which numerous results generated using other approaches are available. We find the same temperature dependence of the Ar_{13} self-diffusion constant that Beck and Marchioro [J. Chem. Phys. **93**, 1347 (1990)] do from their direct calculation of the velocity autocorrelation function: The diffusion constant rises quickly from zero to a liquid-like value as the cluster goes through (the finite-size equivalent of) the melting transition.

I. INTRODUCTION

It frequently has been pointed out that investigations of relatively small clusters offer the promise of an intriguing glimpse into the realm between small molecules and condensed phases.¹ The fact that theoretical calculations on clusters show clear signs of what would be interpreted in a bulk system as melting,²⁻⁴ for example, has been taken as evidence that there is information on phase transitions to be garnered from such studies. The ability to extract this information from experiments, however, depends critically on understanding just what properties of the microscopic clusters one could look for that eventually would develop into the bulk phenomena.

One amply precedented way to proceed would be to consider clusters doped with some chromophore. Changes in the spectroscopy of the chromophore could then be used to explore the evolution of the clusters. Indeed, there have been a number of important experiments reported that do just that,⁵⁻⁷ but, unfortunately, inserting a probe molecule into a small cluster is not an innocuous step. As has now been discussed several times in the literature, clusters have such a high surface-to-volume ratio that changes in the probe spectra are as likely to result from the probe sampling distinctive environments in a single kind of cluster as they are to result from the evolution of a cluster with energy or temperature.^{7,8}

An alternate approach that has been suggested recently is to look at the "phonon spectra" of the clusters.^{4,7,9} Studies along these lines not only would be noninvasive, the reasoning has gone, but they could offer a real opportunity to monitor the dynamics of the clusters. As of yet there have not been any direct infrared or Raman measurements on neat clusters

containing more than a few atoms, but the distribution of vibrational frequencies of a cluster can be accessed theoretically either by doing molecular dynamics and then Fourier transforming the velocity autocorrelation function,⁹ or by calculating what has been called the *instantaneous normal mode spectrum* from, for example, a Monte Carlo (MC) simulation.^{4,7} In the latter approach one diagonalizes the Hessian (the matrix of second derivatives of the potential) and averages the resulting distribution of eigenvalues over the equilibrium distribution of cluster geometries to obtain the desired spectrum.

These theoretical vibrational studies already have begun to yield information about cluster melting. One knew from statistical mechanical considerations that a microscopic number of atoms could not rigorously exhibit a thermodynamic phase transition, but there seemed to be no reason why a sharp *dynamical* signature of melting—such as one might see in the phonon spectra—could not be observed even in a small cluster. In fact, one does find such a signature. It is possible to use the phonon spectrum to compute a diffusion constant for clusters in perfect analogy with one of the ways it can be done in the bulk, through the zero-frequency component of the velocity autocorrelation function's power spectrum.¹⁰ When they performed just such a calculation for Ar_{13} , Beck and Marchioro⁹ found that this diffusion constant drops abruptly from a liquid-like value to (effectively) zero at a well-defined temperature. The fact that precisely this same behavior is also found in bulk freezing is strong evidence that these spectra can indeed provide a useful vehicle for interpolating between microscopic and macroscopic regimes.

Ideally, one would like to be able to arrive at the same diffusion constant from an instantaneous normal mode anal-

ysis. Since they arise from a completely equilibrium calculation, the instantaneous normal modes provide information (such as the so-called Einstein frequency)¹¹ that is complementary to that derived from molecular dynamics; if one is going to be calculating this spectrum anyway, it would be useful not to have to do a separate calculation to obtain diffusion constants. However, the first simple estimates of diffusion constants derived from the instantaneous normal modes were only qualitatively accurate.⁴ They predicted the correct location of the melting temperature, but not the sudden loss of diffusive motion below the freezing point.

There is a problem in principle to be confronted here, namely that diffusion constants are fundamentally long-time results, whereas the instantaneous normal modes (as the name itself suggests) have a rigorous meaning only at short times. Nonetheless, in this paper we show that there is enough information in the instantaneous normal mode spectrum to let us extract reasonably accurate cluster diffusion constants. A straightforward application of the recent theoretical work by Madan, Keyes, and Seeley¹² on diffusion in liquids enables us to compute diffusion constants in substantial agreement with the molecular dynamics results of Beck and Marchioro.⁹ We describe this procedure in Sec. II.

Perhaps, not surprisingly, the success of this approach depends strongly on having the low-frequency portion of the instantaneous-normal-mode spectrum given as accurately as possible. One consequence of this fact is that our previous calculations, which studied clusters that were both rotating and vibrating, would be insufficient for the present purposes. The presence of rotations introduces low-frequency modes that complicate the investigation of the body-fixed-frame diffusion one wants to understand. In Sec. III, therefore, we first identify and then show how to remove these rotational contributions. The formalism of Secs. II and III is illustrated in Sec. IV with a few applications to argon clusters. Some comments on the implications of these results then are given in the final section.

II. INSTANTANEOUS NORMAL MODES AND THE CALCULATION OF DIFFUSION CONSTANTS

The instantaneous normal mode concept already has been discussed in a number of rather different contexts in the literature.^{4,11-14} However, the underlying philosophy is independent of the specific application. At any instant of time the configuration of a system of N atoms in three dimensions can be described by the $3N$ -dimensional vector \mathbf{R}_0 . We can imagine describing the configuration \mathbf{R} of the system a short time later by expanding the potential energy

$$V(\mathbf{R}) = V(\mathbf{R}_0) - \mathbf{F}(\mathbf{R}_0) \cdot (\mathbf{R} - \mathbf{R}_0) + \left(\frac{1}{2}\right)(\mathbf{R} - \mathbf{R}_0) \cdot \mathbf{d}(\mathbf{R}_0) \cdot (\mathbf{R} - \mathbf{R}_0),$$

where $\mathbf{F}(\mathbf{R}_0)$ is the force acting on the system at \mathbf{R}_0 and the elements of the $3N \times 3N$ dynamical matrix $\mathbf{d}(\mathbf{R}_0)$,

$$[\mathbf{d}(\mathbf{R}_0)]_{j\mu, kv} = \frac{\partial^2 V}{\partial r_{j\mu} \partial r_{kv}} \quad (j, k = 1, \dots, N; \mu, \nu = x, y, z),$$

are second derivatives of the potential with respect to the

Cartesian components of the atomic position vectors \mathbf{r}_j . For N identical atoms of mass m , the eigenvectors of the mass-weighted version of this matrix

$$\mathbf{D}(\mathbf{R}_0) = m^{-1} \mathbf{d}(\mathbf{R}_0),$$

are the instantaneous normal modes of the system when it is at configuration \mathbf{R}_0 , and the eigenvalues ω_α^2 , $\alpha = 1, \dots, 3N$, are the squares of the instantaneous normal mode frequencies at that same configuration. The final normal mode spectrum is then calculated by averaging the distribution of frequencies over the equilibrium set of configurations.

We use the adjective "instantaneous" throughout to emphasize the fact that the validity of the harmonic expansion of the potential rests solely on the assumption that one is considering times short enough that \mathbf{R} is close to \mathbf{R}_0 on the average. Since there is no presumption that one is at (or even near) a minimum in the potential, the technique is as well suited for studying fluid-like behavior¹¹⁻¹³ as it is for looking at more conventional vibrations. In fact, the negative eigenvalues of the dynamical matrix (the imaginary frequencies) that arise naturally in this formalism can be interpreted as measures of mechanical instability or fluidity.

By the same token, of course, it would seem that this formalism would have to be ill suited for computing properties that are fundamentally long-time or zero-frequency in character—such as the self-diffusion constant. Still, it is important to remember that the calculation does not simply produce the dynamical information inherent in a short classical trajectory starting from a single initial condition, but rather contains the information embodied in classical trajectories starting from *all* the thermally accessible system configurations. At least formally, one could envision running this ensemble of trajectories in reverse so as to provide data about all the possible modes of relaxation back to the equilibrium distribution of configurations. Thus, in this particular sense, the calculation does have implications for zero-frequency quantities—if only one can find a suitable way of extracting those implications.

One procedure for doing just that was suggested recently by Madan, Keyes, and Seeley,¹² extending some earlier work by Zwanzig.¹⁵ What we have done is adopt this approach fairly literally, subject only to a few modifications that we shall describe shortly. Regardless of the version of the theory employed, the starting point is the Green-Kubo formula giving the self-diffusion constant as a time integral¹⁶

$$D = (k_B T / m) \int_0^\infty C(t) dt, \quad (1)$$

over the normalized velocity autocorrelation function for a single atom

$$C(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle / \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle.$$

One now makes the fundamental assumption that this correlation function has contributions both from a set of stable, relatively local vibrations of frequency ω and from the occasional excursions, with a characteristic frequency ω_v , that take the system away from its stable configurations. If there is a probability distribution $f(\omega)$ that governs the stable vibrations, then we can write approximately that

$$C(t) = \int_0^\infty d\omega f(\omega) \cos \omega t \operatorname{sech} \omega_v t. \quad (2)$$

The reasoning behind this particular form is that the velocity autocorrelation function is required to be an even function of time by Newton's laws, whereas the existence of an excursion frequency ω_v means that the envelope of the simple harmonic $\cos \omega t$ behavior should decay asymptotically as $\exp(-\omega_v t)$. The hyperbolic secant factor allows Eq. (2) to satisfy both criteria. Substituting Eq. (2) into Eq. (1) then yields the working expression

$$D = (k_B T/m) \int_0^\infty d\omega f(\omega) (\pi/2\omega_v) \operatorname{sech}(\pi\omega/2\omega_v). \quad (3)$$

[In previous versions of the theory,^{12,15} the $\exp(-\omega_v t)$ form was used in place of the $\operatorname{sech} \omega_v t$, leading to a slightly different result. For technical reasons having to do with the remainder of the formalism, we find Eq. (3) preferable, but a somewhat generalized formalism that recognizes the possibility of a distribution of excursion frequencies clearly would be preferable to either of these.]

What makes this analysis useful for us is that by exploiting an analogy with the calculations of chemical reaction rates in liquids, Madan, Keyes, and Seeley¹² have derived an expression giving the excursion frequency self-consistently in terms of the diffusion constant,

$$\omega_v = (n/2\pi)(m/k_B T) f_u \langle \omega \rangle_s \langle \omega \rangle_u D, \quad (4)$$

where $\langle \omega \rangle_s$ is the average frequency of the stable-mode vibrations and f_u and $\langle \omega \rangle_u$ are the fraction and the average magnitude, respectively, of the unstable-mode vibrational frequencies. The quantity n represents the number of stable configurational states which are, in some sense, neighbors of a given stable state. That is, it reflects the number of states into which the system can hop.

Obviously, the main ingredient in this formalism is information about the various vibrational modes of our system. In what is another slight variation from earlier work,¹² we shall assume that all of these vibrational properties can be determined directly from the instantaneous normal mode frequencies: $f(\omega)$ will be taken to be the (normalized) distribution of *real* instantaneous normal mode frequencies and the average stable mode frequency will be considered to be the average of these real frequencies. Similarly, the average unstable mode frequency will be the average of the *imaginary* instantaneous normal mode frequencies and f_u the fraction of modes that are imaginary.

The reader is referred to the original derivation for the detailed rationale for this equation,¹² but the reason why the instantaneous normal mode spectrum can provide the necessary input for the calculation is not difficult to see. One is envisioning that for the majority of the time the system finds itself in the stable regions of configuration space, as defined by the presence of a well-defined set of (real) vibrational frequencies. Occasionally, though, the system tries to surmount the barriers separating one stable region from an-

other. When that happens, the rate of passage over the barriers depends, as it does in a chemical reaction, on the attempt frequency (the average real frequency), the curvature of the barriers (the average imaginary frequency), the friction imposed by the surrounding medium (as determined by the diffusion constant), and the number of channels by which the system can leave the stable regions. To the extent to which we believe that the imaginary modes are the primary means by which the system makes large amplitude excursions, the fraction of imaginary modes has to enter into the calculation of this number of channels.

The only undermined quantity at this point is the "coordination number" n . Lacking the kind of nonlocal information about the topography of the potential surface that this n represents, the natural approach is to follow Madan, Keyes, and Seeley¹² and treat n as a parameter to be determined from information outside the formalism. Madan, *et al.*, proceed by first computing the diffusion constant from simulation at one fixed temperature and then assuming that the value of n so obtained can be treated as a temperature-independent constant for purposes of evaluating D at other temperatures. This assumption actually works out quite well, giving diffusion constants for cold, dense, Lennard-Jones liquids in excellent agreement with simulation over the entire range of conditions studied.

There are, however, reasons not to adopt this same implementation procedure. One is that it suggests that a genuine dynamical calculation must somehow be included in order for the formalism to work. It obviously would be more internally consistent to be able to compute all the necessary quantities from equilibrium data. More urgent still is the fact that this implementation actually can fail. Neither Eq. (3) nor its equivalent with an exponential decay function need be solvable for every externally supplied value of D . Indeed, it is easy to verify numerically that the right-hand side of Eq. (3) always reaches a maximum for a particular value of ω_v , so the formalism is unable to accommodate any diffusion constant larger than this maximum.

The approach we shall pursue here obviates both of these problems. At high temperatures it turns out to be possible to estimate the excursion frequency ω_v directly from the instantaneous normal mode data. Unlike the situation with the diffusion constant, there are no limits placed on the possible values of ω_v by Eq. (3). Hence one always can obtain a value for n at some temperature T_0 by solving Eqs. (3) and (4) simultaneously with our estimated $\omega_v(T_0)$. Then, as suggested by Madan, *et al.*,¹² the diffusion constant (and ω_v if desired) can be computed for all lower temperatures by continuing to solve Eqs. (3) and (4) simultaneously with that same value of n .¹⁷

All that is required to come up with an approximate $\omega_v(T_0)$ is to remember that the velocity autocorrelation function implied by the instantaneous normal mode spectrum is exact at short times.^{4,11} That is, the first few coefficients in the Taylor series expansion

$$C(t) = 1 - A_2 t^2 + A_4 t^4 + \cdots,$$

are given exactly by the first few moments of the instantaneous normal mode spectrum:

$$A_2 = \left(\frac{1}{2!}\right)(3N-6)^{-1} \left\langle \sum_{\alpha=1}^{3N-6} \omega_{\alpha}^2 \right\rangle \quad (5)$$

$$A_4 = \left(\frac{1}{4!}\right)(3N-6)^{-1} \left\langle \sum_{\alpha=1}^{3N-6} \omega_{\alpha}^4 \right\rangle,$$

where the sums are over all the real and imaginary modes for each system configuration (minus the translations and rotations) and the averages are over the equilibrium distribution of system configurations. Now, one can rewrite this correlation function so that it remains exact through the same order in time by saying

$$C(t) = \cos at \operatorname{sech} bt,$$

provided we identify the constants a and b correctly in terms of A_2 and A_4 . Comparing this expression with Eq. (2) though, suggests that, at least in an Einstein-like approximation, the constant b is precisely the asymptotic decay frequency ω_v . In other words, it leads us to the high-temperature estimate

$$\omega_v(T_0) = [(3A_4/A_2) - (A_2/2)]^{1/2}. \quad (6)$$

In principle this equation could be used to help evaluate the diffusion constant at all temperatures, but it is only at relatively high temperatures that it is really plausible. It is, after all, only at the highest temperatures that the asymptotic relaxation time ω_v^{-1} will be short enough to be given so directly by the instantaneous normal mode time correlation function. What one really wants is for ω_v^{-1} to be less than the reciprocal Einstein frequency—which has been identified as the rough maximum time for which the instantaneous normal mode dynamics is likely to be accurate.^{4,11} However, this inequality has no choice but to break down as the temperature declines and the relaxation time begins to grow exponentially.

Still, as we shall see in Sec. IV, this estimate does yield reasonably accurate results for the dependence of the diffusion constant on temperature when used in conjunction with Eqs. (3) and (4). One way of understanding this accuracy is to note that the Madan-Keyes-Seeley-Zwanzig formalism^{12,15} is best suited for the low-temperature, activated regime when the stable configurations are well defined because there are relatively few excursions between them. From this perspective the high-temperature information is simply a necessary complement to the low-temperature theory, enabling it to describe the dynamics over a much wider range than otherwise could be possible.

Of course, all of the discussion to this point applies as well to bulk liquids as it does to clusters, so a few words are in order about one of the specific features of clusters. For bulk systems the rotational and translational modes can give no measurable contribution to the normal mode spectrum: in the thermodynamic limit, $3N-6$ modes are indistinguishable from $3N$ modes. With soft clusters, though, the presence of coupling between vibration and rotation can lead to noticeable effects on the lowest magnitude real and imaginary frequencies. Since low-frequency information is the crucial element in understanding diffusion, it may not be surprising that these effects can lessen the accuracy of our computed diffusion constants quite a bit. We therefore will have to

discuss, in the next section, how the consequences of rotation can be removed.

Interestingly, if we were to use the full spectrum of the rotating-vibrating clusters, the resulting low-frequency portion of the spectrum would change completely the qualitative predictions for diffusion behavior. What we shall see in Sec. IV is that, with the corrected spectrum, the diffusion constant drops sharply to zero at a critical temperature and remains zero for all lower temperatures. Such an occurrence is permissible mathematically because Eqs. (3) and (4) always have $D = \omega_v = 0$ as a solution, provided that $f(\omega = 0) = 0$. Below the critical temperature it turns out that this solution is, in fact, the only root of the simultaneous equations. If the zero-frequency component of the spectrum, $f(\omega = 0)$, does not have zero weight, though, the right-hand side of Eq. (3) always contains a finite contribution, even in the limit that $\omega_v \rightarrow 0$. Including the rotations would give such a finite zero-frequency component, so the diffusion constant would show a kink at a critical temperature but would never drop to zero at any finite temperature.

III. CLUSTER ROTATIONS

As we indicated in the previous section, the calculation of accurate self-diffusion constants requires that there be no extraneous low-frequency contributions to the instantaneous normal mode spectrum arising from the overall rotations of the cluster. To see where rotations enter the spectrum in the first place, consider the elementary case of a homonuclear diatomic molecule modeled as a rotating simple harmonic oscillator, for which the potential energy function is just

$$u(r) = \left(\frac{1}{2}\right)k(r-r_0)^2,$$

where k is the force constant, r is the diatomic bond length, and r_0 is the equilibrium value of r . It is now a simple matter to write down the full 6×6 dynamical matrix for this system and to solve for the frequencies of the motion analytically. Specifically, we need, following the prescription of Ref. 4,

$$t_{\sigma}(r) = -u''(r) = -k$$

$$t_{\pi}(r) = -u'(r)/r = -k(1-r_0/r) \equiv -k\xi,$$

and taking r to lie along the z -axis, we find that the mass-weighted dynamical matrix is just

$$D = \frac{k}{m} \begin{pmatrix} \xi & 0 & 0 & -\xi & 0 & 0 \\ 0 & \xi & 0 & 0 & -\xi & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 \\ -\xi & 0 & 0 & \xi & 0 & 0 \\ 0 & -\xi & 0 & 0 & \xi & 0 \\ 0 & 0 & -1 & 0 & 0 & 1 \end{pmatrix}.$$

The eigenvalues of D then are obtained in the usual manner, namely by solving for the roots of the characteristic polynomial associated with the equation $\det[D - \lambda I] = 0$, which in this particular case factors to yield

$$\lambda^3(\lambda - 2\xi)^2(\lambda - 2) = 0.$$

Consequently, the six frequencies of the motion deriving from the rotating simple harmonic oscillator are seen to be

$$\begin{aligned}\omega &= 0, 0, 0, \sqrt{2\xi k/m}, \sqrt{2\xi k/m}, \sqrt{2k/m} \\ &= 0, 0, 0, \omega_0 \sqrt{1 - (r_0/r)}, \omega_0 \sqrt{1 - (r_0/r)}, \omega_0\end{aligned}$$

where $\omega_0 = \sqrt{2k/m} = \sqrt{k/\mu}$, μ being the reduced mass of the homonuclear diatomic.

When the oscillator is undisplaced, i.e. when $r = r_0$, note that the degenerate pair of eigenvalues vanish, leaving $\omega = \omega_0$ as the only nonzero frequency. The more general result, though, is that the diagonalization of the dynamical matrix in the full six-dimensional space of the system yields three zero-frequency modes corresponding to overall center-of-mass translation, two degenerate modes of frequency $\omega = \omega_0 \sqrt{1 - (r_0/r)}$ which are implicit functions of the instantaneous system configuration, and an additional mode which is independent of the oscillator displacement and which is the only nonzero frequency obtained when the problem is solved in the space of reduced dimensionality corresponding to a nonrotating system. We should note that this result is by no means a special feature of a harmonic system, but rather is characteristic of the rotating diatomic in general. One easily can show that the frequencies of a homonuclear oscillator are of the form

$$\omega = 0, 0, 0, \sqrt{u'(r)/\mu r}, \sqrt{u'(r)/\mu r}, \sqrt{u''(r)/\mu}$$

with the degenerate pair of frequencies tending towards zero only when the forces on the atoms vanish, that is when the diatomic is found near the minimum of its potential well. At low temperatures the oscillator will be found on the average near this potential minimum, and so rotational contributions to the instantaneous normal mode spectrum will become negligible in this limit. The effect cannot be ignored, however, at higher temperatures. (In the limit $T \rightarrow \infty$, one finds in the harmonic oscillator case that $\langle 1 - (r_0/r) \rangle \rightarrow 1$, i.e. the rotation-induced frequencies are of the same magnitude as the configuration-independent frequency.) A prescription for identifying and extracting these spurious frequencies therefore must be implemented if we are to generate quantitative predictions of the low frequency dynamics.

Formally the process of removing the rotational contributions to an instantaneous normal mode spectrum is quite straightforward in the limit of no vibration-rotation coupling. One simply uses standard techniques for projecting out the rotational contamination of the full dynamical matrix, so that one is left with the diagonalization of a projected dynamical matrix in order to obtain the correct frequency spectrum.^{14,18} Specifically, this $3N \times 3N$ projected matrix D^P is defined in terms of the unprojected matrix by the expression

$$D^P = (1 - P) \cdot D \cdot (1 - P)$$

where the projector P , which separates out the rotational degrees of freedom, has elements given by

$$P_{i\mu, j\nu} = \sum_n l_{i\mu, n} l_{j\nu, n}$$

Here n runs over the indices of the three (two, if the cluster is linear) independent unit vectors l of dimension $3N$ that describe the infinitesimal rotations of the cluster, while the indices labeling the components of P are the same ones which

are appropriate to D , namely $i, j = 1, \dots, N$ and $\mu, \nu = x, y, z$. (This analysis also can be extended to the treatment of the overall translation of the cluster. However, the procedure for generating cluster configurations does not couple center-of-mass and internal motions, and thus the diagonalization of D itself always yields the required three zero eigenvalues corresponding to the translational degrees of freedom.) In the absence of vibration-rotation coupling, these $\{l_n\}$ are just three (again, two for a linear cluster) of the eigenvectors arising from the diagonalization of D , so the projection procedure is completely equivalent to dropping those frequencies, which in practice are small in absolute magnitude, that correspond to the rotational eigenvectors.

When there is a coupling of rotational and vibrational degrees of freedom, one finds that the set of eigenvectors of D does not include exactly three purely rotational $\{l_n\}$, but instead most or all of these eigenvectors involve mode mixing to some extent. Nonetheless it is possible to effect an approximate removal of the rotational contributions by identifying the three eigenvectors of D having the largest rotational components and using them in the projection scheme. This identification begins by recognizing that each eigenvector corresponds to a unit velocity vector describing the relative directions of the motions executed by the cluster atoms when that particular degree of freedom is excited. Such motion then would be associated with an overall angular momentum, whose magnitude is

$$L_n = c \left| \sum_{i=1}^N m_i (\mathbf{r}_i \times \mathbf{l}_{i,n}) \right|$$

where \mathbf{r}_i is the position vector of the i th atom (having mass m_i) and $\mathbf{l}_{i,n}$ is the corresponding contribution to the n th cluster instantaneous normal mode. The constant c appearing here accounts for the magnitude of the overall cluster rotational velocity (recall that the $\{l_n\}$ are unit vectors). For a given cluster configuration, the three modes n displaying the largest L_n values are the ones included in the projector, and thus it is their eigenvalues which are removed prior to calculation of the self-diffusion constant.

To demonstrate the utility of the above approach, we focus briefly on the distributions of angular momentum values associated with instantaneous normal mode eigenvectors of particular prototypical systems. In doing so we resume the examination of the small argon clusters which attracted our attention in two previous investigations; the interested reader is referred to the published descriptions of those investigations for the full details of the calculations.^{4,7} Here it is sufficient merely to note that equilibrated representative cluster configurations can be obtained easily (as long as the equilibrium temperature is not so high that particle evaporation presents a serious problem) via isothermal MC techniques,¹⁹ and that these configurations constitute the set of points about which the system potential energy is expanded. In the upper panel of Fig. 1, we report the normalized distribution of L_n for Ar_{13} clusters at three temperatures (10, 30, and 40 K) representing qualitatively different dynamical regimes (solid-like, transition, and liquid-like regimes, respectively). The scaling of the angular momenta here is somewhat arbitrary, since we have omitted both the particle mass

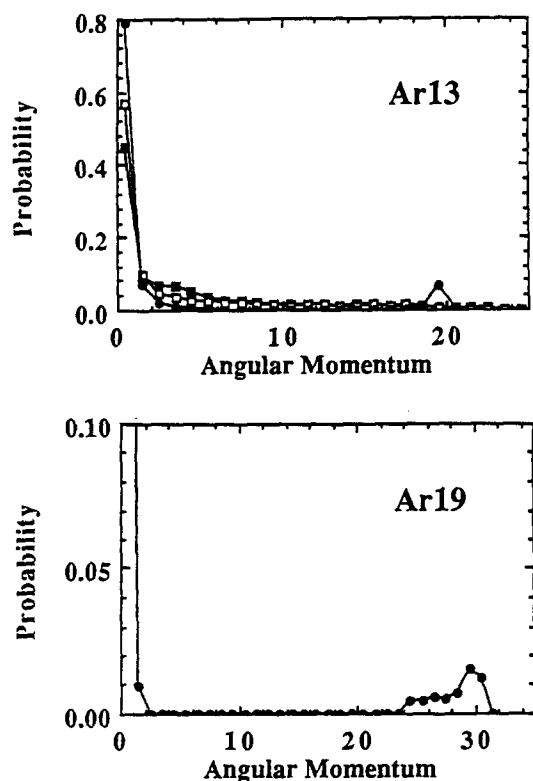


FIG. 1. Normalized distributions of instantaneous normal modes L_n ("angular momenta"). Upper panel: results for Ar_{13} at 10 K (filled circles), 30 K (open squares), and 40 K (filled squares). Lower panel: detail of the results for Ar_{19} at 2 K.

and the magnitude of the overall rotational velocity, this latter quantity not being obtainable from an MC calculation. Note that at all three temperatures the distribution is strongly peaked about zero, a result indicating that most of the eigenvectors obtained by diagonalizing D are not affected seriously by the rotational artifacts. The contamination problem does appear to become more severe as the temperature increases, but this effect turns out to be of little practical importance in the calculation of the self-diffusion constant. At higher temperatures, where the cluster is more fluid and consequently the self-diffusion constant is larger, the low-frequency modes no longer play a dominant role in determining the value of D , that role passing to the moments of the overall frequency spectrum. At the lowest temperature considered here (10 K), the width of the peak at zero angular momentum is very narrow, however one also finds that a new narrow feature appears in the distribution at a relatively large value of L_n . The area of this new peak suggests that of the thirty-nine eigenvectors obtained for each Ar_{13} configuration, only three of these are associated with non-negligible rotational angular momentum. This is, of course, exactly the behavior one expects to observe whenever there is a relatively clean separation of rotational and vibrational degrees of freedom, with the narrow width of the finite angular momentum peak being consistent with the 13-atom clusters existing in the minimum-energy, highly symmetric, icosahedral geometry. We also have calculated the moments of inertia of these same configurations and have found the nar-

row distribution characteristic of a single, spherically symmetric structure.

Low-temperature Ar_{19} clusters, which are known to be polyicosahedral,²⁰ should be characterized by a slightly different angular momentum distribution, in that the moment of inertia about the long axis of the cluster is not equal to the two perpendicular moments. In fact, the distribution of moments of inertia calculated using representative configurations of these clusters does indeed exhibit the expected bimodal shape. The lower panel of Fig. 1 shows the angular momentum values corresponding to the eigenvectors obtained for this system. Note that the distribution of nonzero angular momenta has two components, one of which (the one at the highest L_n) is roughly twice the size of the other. So again we observe structure in the angular momentum distribution which may be understood in terms of the basic geometry of the cluster. But more importantly, we find there to be an automatic approximate segregation of rotational and vibrational modes which indicates that the simple prescription described above for removing extraneous rotational contributions should be quite adequate.

IV. RESULTS AND DISCUSSION

A. Rotationless spectra

Prior to presenting our calculated self-diffusion constants for small argon clusters, we want to indicate the effects on the instantaneous normal spectra due to projecting out extraneous rotational contributions by means of the procedure described in Sec. III. The spectrum computed for Ar_{13} at 10 K is given in Fig. 2 along with the one which would be generated if no such removal were attempted. (This latter spectrum is the same one reported in Ref. 4). One immediately sees that the greatest differences between the two spectra occur when the absolute magnitude of the frequency is small. Not only is the spurious low-frequency peak in the real frequencies absent in the projected spectrum, but the peak in the imaginary frequencies essentially disap-

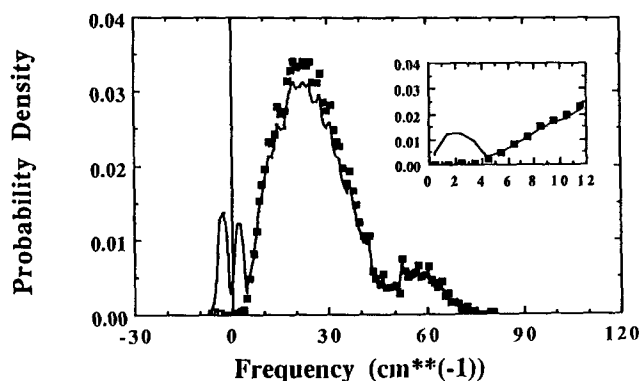


FIG. 2. Instantaneous normal mode spectra for Ar_{13} at 10 K. The points are calculated using the method described in the present work, while the solid line represents the spectrum obtained using the method of Ref. 4. (For convenience, imaginary frequencies are plotted on the negative frequency axis.) The inset graph is an expansion of the results calculated at very low real frequencies.

pears as well. Clearly the imaginary frequencies obtained at this temperature are almost exclusively artifacts of the inclusion of rotational degrees of freedom. That they do not survive the projection procedure is quite reasonable, of course, since at this temperature one does not expect the cluster to sample configuration space near the tops of the barriers separating adjacent potential wells. Note that there is no appreciable change in the higher-frequency portions of the spectrum, and in particular that the feature near 60 cm^{-1} attributed previously to an interior vibrational mode (i.e., the vibration of the one atom lying in the interior of the icosahedron) is unchanged.

We compare now this result obtained at a low cluster temperature with one deriving from a calculation performed at 40 K, a temperature at which the cluster dynamics is liquid-like. (See Fig. 3.) Again we observe the disappearance of the low-frequency spike, but this time very little concurrent change is seen in the distribution of imaginary frequencies. These imaginary frequencies are not artifacts here, but instead are indicative of facile structural rearrangements which are possible when there is sufficient energy that motion is not largely confined to oscillations within discrete potential wells.

Interestingly, the removal of rotations also allows us to observe the gradual growth of the long-wavelength modes of these clusters as the cluster size is increased. The insets in Figs. 2 and 3 reveal that even with as few as 13 atoms, the low-frequency portion of the density of states is beginning to resemble a Debye spectrum (that is, to be proportional to ω^2), despite the fact that the Debye form is derived by assuming an infinite system.²¹ The major deviation from the Debye form evident in these figures is that, unlike a bulk solid, the finite rigid clusters must have a nonzero minimum frequency.

B. Diffusion Constants

We begin by comparing self-diffusion constants calculated in the manner described herein with the values obtained using other methods. Again Ar_{13} is taken as the example system, with the results of these calculations being displayed in Fig. 4. D is found to be identically zero below a temperature of about 27 K, but just above this temperature

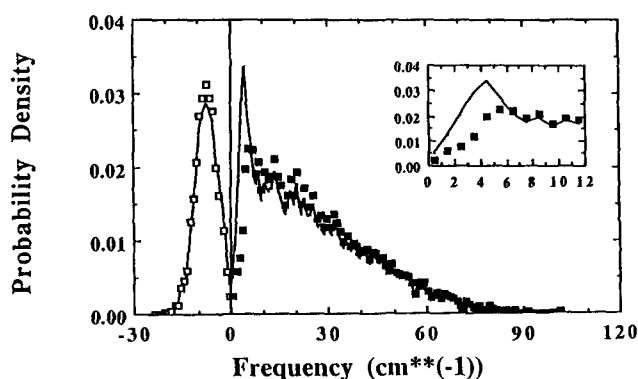


FIG. 3. Instantaneous normal mode spectra for Ar_{13} at 40 K. The symbols have the same meanings as in Fig. 2.

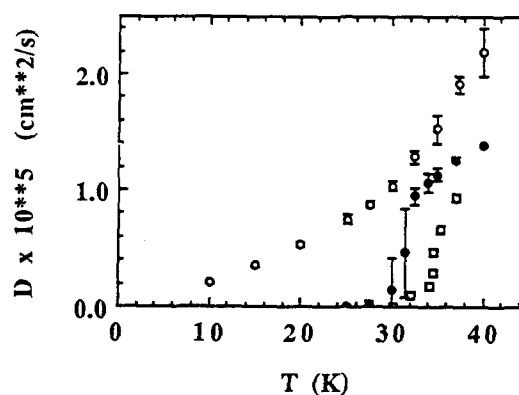


FIG. 4. Temperature dependence of the self-diffusion constant for Ar_{13} as given by three different methods: the present formalism (filled circles—the error bars represent one standard deviation); the method of Ref. 4 (open circles), which is based solely on moments of the instantaneous normal mode spectra; and the time dependence of the mean square particle displacement (open squares) as calculated by Beck and Marchioro (Ref. 9).

there is a sharp rise occurring over a 4–5 K range. Although in this transition region there is a relatively large uncertainty associated with the points (the error bars in fact reflect the real differences in the behavior of individual clusters at these temperatures—some of the clusters are strictly solid-like while others are becoming more fluid), the shape of the curve is consistent with the onset of an activated process. The quantitative difference between this curve and the one we reported previously⁴ (and which is reproduced in Fig. 4) obviously are great; those earlier values, calculated from the moments of the entire frequency spectrum, are nonzero at all finite temperatures. Nonetheless, there is a very important qualitative agreement between the two sets of results, namely that they both clearly signal the dynamical transition occurring in these clusters in the vicinity of 30 K.

There is a much better quantitative agreement between our latest results and those calculated by Beck and Marchioro,⁹ which also display a sigmoidal temperature dependence. Those workers obtained values of D both from the slope of the mean square particle displacement and also from the zero-frequency component of the velocity autocorrelation function, with a system temperature being computed from the average value of the kinetic energy. The only significant difference between our results and theirs is the shift of their curve by roughly 4 K to higher temperatures, but this shift is easily understood on the basis of the different ensembles represented in the two sets of calculations. For small systems it is well known that different statistical ensembles actually correspond to different experimental determinations, and so it is not valid to compare directly the results stemming Beck and Marchioro's isoergic⁹ and our isothermal calculations. Nevertheless, it is significant that the discrepancy is exactly in the direction one would expect, namely that our results, which include the influences of sampling higher energy configurations, indicate an earlier onset of cluster melting. This result is not unlike what one finds for a simple bimolecular collision reaction: since the rate of the reaction is dominated by the kinetics of those collisions occurring with just enough energy to overcome the activation

barrier, the high-energy tail of a thermal energy distribution can be responsible for the initiation of reaction even though the average energy itself may not exceed the barrier.

We also have calculated self-diffusion constants for the other argon clusters which we examined in our earlier work.^{4,7} In Fig. 5 one finds the results of those calculations for Ar₇, Ar₈, and Ar₁₉ (as well as those for Ar₁₃). The most important generalization of the behavior revealed in this plot is the most obvious one, that for each of these clusters there is a temperature below which there is no observed diffusion and thus below which the cluster dynamics is typical of a solid. Above this temperature at which melting begins, there is a transition region on the order of 4–6 K in width over which D increases sharply and beyond which D displays a more gradual, essentially linear increase with temperature. This ultimate temperature dependence appears on the basis of these limited results to be a general characteristic of argon clusters, since the slopes of the four curves in the liquid-like dynamical regime are very similar. Given the necessarily large error bars associated with the diffusion constants in the transition region, it is difficult to draw many firm conclusions about the cluster size dependence of the melting transition. However, one does find a much greater difference between the onset of melting in, say, Ar₇ and Ar₁₃ than in Ar₁₃ and Ar₁₉, even though in each case the larger cluster has 6 more atoms than the smaller cluster. This result derives from the structural similarity of the solid-like 13-atom and 19-atom clusters (the 19-atom cluster is essentially just an extension in one dimension of the smaller cluster) in which there are both surface and interior argon bonding sites, in contrast to the rigid 7-atom and 8-atom clusters which involve only surface sites.

The results of Figs. 4 and 5 make a very important point concerning the general utility of the instantaneous normal mode analysis of cluster dynamics as an approach to the calculation of self-diffusion constants. It might be argued that since diffusion of atoms within a cluster is inherently a long-time process, any formalism which is fundamentally based on a correct analysis of the short-time dynamics necessarily must be inadequate. In support of such a viewpoint,

one might point to the lack of quantitative agreement between our previous results and those derived from recent trajectory calculations of Beck and Marchioro⁹ and suggest that this disagreement must arise from underlying problems with the approach. The present calculations have demonstrated, though, that this previous disagreement does not arise from a basic inadequacy of the instantaneous normal mode method itself but rather from the use of an expression for the diffusion constant which is relatively insensitive to the low-frequency part of the phonon spectrum. By adopting a superior model of the velocity autocorrelation function and making use of the entire frequency spectrum, we in fact can obtain an expression for D that yields results which are comparable with those computed by other means.

V. CONCLUDING REMARKS

In the present work we have described a method for generating self-diffusion constants for atoms in small clusters on the basis of the information contained in the instantaneous normal mode spectra of those clusters. Not surprisingly, the ability to extract quantitative values of the diffusion constant depends sensitively on the low-frequency structure of such spectra and therefore requires the removal of spurious rotational contributions. (These rotational effects can be seen to be an unavoidable consequence of treating the full dimensionality of the system, vanishing only in the limit that motion of the cluster is either strictly harmonic or macroscopic.) When the method is applied to the study of several small argon clusters, the values obtained are found to be in good agreement with those calculated via molecular dynamics techniques⁹ and reveal the unmistakable signature of the dynamical transition which is the cluster analog of bulk melting.

Given that the formalism used to perform these calculations differs slightly from that proposed by Madan, Keyes, and Seeley,¹² it may be worthwhile to comment, at least briefly, on the significance of these differences. The variation in the approach to the initial high-temperature input to the equations is largely a technical change, albeit an important

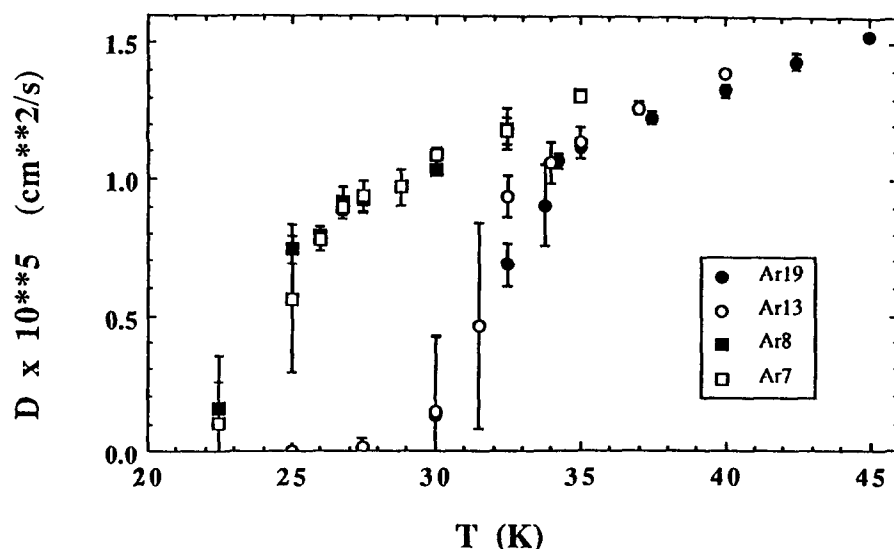


FIG. 5. Temperature dependence of the self-diffusion constant for several small argon clusters, as determined by the methods of the present work.

one for practical solutions. Somewhat more interesting, though, is the direct use of instantaneous normal mode data instead of the "quenched" distribution advocated by Madan, *et al.*, for characterizing the stable modes. Those authors suggest that the transitions from one stable configurational state to another be interpreted as jumps between the Stillinger-Weber minima^{20,22} of the system. Under this assumption the stable mode vibrations would then have to be computed from some zero-temperature (quenched) set of configurations—and one certainly would not want to include the high frequency tail of the spectrum associated with particles being high up on the repulsive wall of the pair potentials. However, except at the lowest temperatures, a fluid-like system usually will not be particularly close to any of the Stillinger-Weber minima; more typically a finite-temperature system will be found in regions that are not wells at all since motion along some of the coordinates is unstable. Because of this fact, we think the idea of a stable region can be viewed a bit more broadly—and that the real instantaneous normal modes very well might be an appropriate way to characterize these regions. In support of this idea that the concept of a stable region be taken less literally, we note that our value for the parameter n (the number of neighboring stable regions) actually would vary somewhat if we were to vary the choice of our initial temperature T_0 .²³

Perhaps the most significant aspect of this study is that it reconfirms the usefulness of the instantaneous normal mode method as a means for monitoring the dynamics of systems of arbitrary size. One would like, therefore, to use this method as a departure point for the development of techniques for simulating actual spectroscopic results. The first step in this direction, the generation of infrared spectra, is likely to be relatively straightforward: the instantaneous normal mode spectra (representing, of course, vibrational densities of states) provide the input into the construction of the requisite dipole correlation functions. Far less obvious, however, is the proper way of including this vibrational information in simulations of electronic spectra. The achievement of that end would result in a link being forged between the current calculations and recent experimental probes of cluster dynamics based on changes in the electronic spectrum of an added chromophore.^{5,6} Actually, it is possible that only calculations such as these may yield the precise correlation between the internal dynamics of the cluster atom "solvent" and the perturbation of the chromophore's spectrum that would allow one to refine contemporary broad characterizations of the interactions in terms of wetting and nonwetting structures.^{6,7}

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