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# Instantaneous normal mode analysis as a probe of cluster dynamics

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We report an analysis of dynamical transitions in small argon clusters based on a study of the vibrational frequencies (photon spectra) of these systems. Even in the liquidlike regime such an analysis can be shown to provide an exact description of the short-time cluster dynamics and represents an alternative to more conventional strategies which concentrate on an enumeration of minimum energy structures. The overall picture of "melting" transitions emerging from this study is one of a series of isomerizations which preserve the short-range structures of the clusters, with the structures linked by these isomerizations sometimes being far from any of the local minima on the potential energy hypersurface. As a part of the analysis, we describe a general method for estimating cluster atom self-diffusion constants from system configurations obtained via either isothermal or isoergic Monte Carlo calculations.

## I. INTRODUCTION

Much of the success of chemical physics is due to its willingness to focus on the behavior of individual atoms and molecules. Yet there are intriguing phenomena associated with matter in bulk that can only arise from many molecules acting in concert. One such phenomenon, which will concern us in this paper, is the occurrence of distinct thermodynamic phases separated by sharp phase transitions. The existence of well-defined liquid and solid phases, e.g., means that bulk materials can melt and freeze. However, this apparently clean separation between microscopic and macroscopic behavior leaves open the question of what can happen to the melting process with fewer than a mole of atoms. Unfortunately, neither studies of few molecule systems nor probes of  $10^{23}$  molecule systems will tell us how phenomena such as melting manage to interpolate between these two regimes.

It is the desire to delve further into the origin of bulk macroscopic behavior, among other reasons, that has prompted the considerable experimental emphasis being placed on the investigation of small clusters.<sup>1-3</sup> The feeling is that by following the evolution of phenomena such as melting as the number of atoms in the cluster is increased, one will begin to learn how purely bulk properties arise.<sup>4</sup> There are, however, a number of problems with this approach. One set of problems is experimental; it is difficult to know what to monitor in order to see a cluster melt. Indeed, it is only relatively recently that there have been experiments capable of addressing this issue in any direct fashion.<sup>5,6</sup>

Perhaps more fundamentally, there are difficulties on the theoretical side as well. It is by now well known that there is a definite transition between liquidlike and solidlike behavior in small clusters as a function of temperature (and of energy).<sup>4,7-20</sup> Yet, it is a mathematical fact that thermodynamic phase transitions cannot occur in a finite system. In

order to have a true phase transition, there must be some nonanalyticity in the partition function, but there is just no mathematical mechanism for generating nonanalytic behavior out of integrals and exponentials of (well-behaved) potentials unless the number of particles is effectively infinite—i.e., unless the system is macroscopic.<sup>21,22</sup> That being the case, what can the behavior be that actually does evolve into the phase transition?

This very question is one that has been put forth countless times in the literature.<sup>23</sup> Some of the earliest work claimed that there were sharp transitions even for clusters of a few Ar atoms.<sup>9</sup> It was soon realized that the actual simulation that gave rise to this observation was insufficiently relaxed (a problem that has continued to haunt cluster simulations),<sup>11</sup> but the possibility of the existence of other sharp transitions (in particular, sharp separated melting and freezing transitions) is still being raised by statistical mechanical models,<sup>13,20</sup> despite the impossibility of such transitions being there in any *rigorous* sense.

In a way, the discussion itself has embodied the conflicting perspectives of the macroscopic and microscopic regimes. The desire to think of 13, or even seven, Ar atoms as being able to melt is clearly the result of a macroscopic viewpoint. On the other hand, much of the analysis in the literature has been exclusively microscopic in outlook. At the outset, a great deal of the emphasis was on simply listing the possible potential-energy minima for a given cluster, much as though these clusters were small molecules in a quantum chemistry calculation.<sup>1</sup> It is far from obvious, however, that these minima have any bearing on experiments done at non-zero temperatures (except in the case of the so-called magic number clusters).<sup>17,18</sup> This basic strategy has been refined in recent years so as to concentrate on the "inherent structures" underlying the various finite temperature configurations.<sup>11,15,18</sup> Nonetheless, when attempts are being made to identify specific mechanisms by which the cluster can isomerize from one inherent structure to another, the perspective is clearly still a small molecule one.

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All of this is not to say that either of these ways of thinking is incorrect. Both have contributed to our current level of understanding. The macroscopic viewpoint has clarified the importance of long equilibration times (especially near the transition region) and has emphasized that constant energy and constant temperature calculations have every right to give different answers.<sup>11</sup> Different ensembles correspond to different experiments for a small system. The microscopic studies have pointed out the ubiquity of structures with five-fold symmetries, such as polyicosahedra and Mackay icosahedra, and of the role of these 0 K structures in understanding why properties can change nonmonotonically with cluster size.<sup>11,17,18</sup>

What is still needed in order to meet the original goal of understanding the evolution of cluster behavior with size though are concepts that are equally valid at both the microscopic and the macroscopic ends of the scale. There should be some set of properties one can follow from 2 to  $10^{23}$  atoms that is both well defined and practical at every step along the way. What we wish to suggest in this paper is that a reasonable approach would be to look at neither the equilibrium properties nor (*a fortiori*) at ground-state geometries, but rather at the *dynamics* of the clusters.<sup>19</sup> We feel that this idea is a promising one for several reasons. For one thing, the prohibition against a few-degree-of-freedom system having a sharp transition is only true for equilibrium transitions, not for dynamical ones. Indeed, there are numerous examples of transitions in the nature of the dynamics occurring for as few as two coupled oscillators.<sup>24</sup> A second and more telling point is that the most likely experimental signatures of melting will be dynamical. In all probability, the best experimental data one will be able to garner will be in the form of line broadenings, a probe of the relaxation time of the cluster.<sup>6</sup>

The particular dynamical quantities we shall examine in this paper are the *vibrational frequencies* of the cluster. A well-defined set of frequencies obviously exists for a rigid cluster of any size, but what makes this idea useful to us in the context of melting is that it turns out to be possible to discuss the vibrational frequency spectrum of a liquid as well as that of a solid. One can define a set of *instantaneous normal modes* that do not require that the system be at, or even near, some equilibrium geometry.<sup>25,26</sup> Moreover, it is possible to show that the distribution of these modes can give us information on the self-diffusion constant of the atoms in the cluster and thus a direct measure of the fluidity of our clusters.

In the next section, we shall review the instantaneous normal mode concept, pointing out, in the process, the various guises in which much the same idea has appeared in the literature.<sup>8,14,16-19</sup> We then discuss how we can calculate this spectrum by Monte Carlo simulations (both at constant temperature and at constant energy). Section IV illustrates these ideas with simulations of a few, well-studied, small Ar clusters and we conclude, in Sec. V, with some general remarks.

## II. INSTANTANEOUS NORMAL MODES

The normal vibrational modes of a crystalline solid are just as simple to think about as the normal vibrational modes

of a small molecule are. Indeed, the two sets of frequencies can be computed in much the same way.<sup>27,28</sup> If there are  $N$  atoms in the system, there are  $3N$  Cartesian coordinates

$$r_{j\mu} \quad (j = 1, \dots, N) \quad (\mu = x, y, z).$$

So, one can always set up a  $3N \times 3N$  force-constant matrix from the second derivatives with respect to these coordinates of the potential  $V$  (properly mass-weighted),

$$D_{j\mu, k\nu} (m_j m_k)^{-1/2} \frac{\partial^2 V}{\partial r_{j\mu} \partial r_{k\nu}}. \quad (2.1)$$

Here  $m_j$  and  $m_k$  are the masses of the  $j$ th and  $k$ th atoms. If these derivatives are evaluated at the global minimum of the potential, then the  $3N$  eigenvalues of this matrix are

$$\omega_\alpha^2, \quad (\alpha = 1, \dots, 3N),$$

the squares of the  $3N$  normal mode frequencies.

For the examples of interest to us in this paper, the total potential energy can be expressed as a sum over pair potentials

$$V = \sum_{\substack{j,k \\ (j < k)}} u(r_{jk}),$$

(with  $r_{jk}$  the distance between the  $j$ th and  $k$ th atoms), so that the dynamical matrix  $D$  can be written in terms of the derivatives of the pair potentials,

$$\begin{aligned} t_\sigma(r) &= -u''(r), \\ t_\pi(r) &= -u'(r)/r. \end{aligned} \quad (2.2)$$

Explicitly,

$$\begin{aligned} D_{j\mu, k\nu} &= (m_j m_k)^{-1/2} \left\{ \left[ \frac{(r_{j\mu} - r_{k\mu})(r_{j\nu} - r_{k\nu})}{r_{jk}^2} \right] \right. \\ &\quad \times [t_\sigma(r_{jk}) - t_\pi(r_{jk})] + \delta_{\mu\nu} t_\pi(r_{jk}) \Big\}, \quad (j \neq k) \\ D_{j\mu, j\nu} &= - \sum_{l \neq j} D_{j\mu, lv} (m_l/m_j)^{1/2}, \quad (j = k). \end{aligned} \quad (2.3)$$

This simple development can be extended in a number of ways. In either an amorphous solid or a liquid, the material would have a distribution of possible atomic arrangements. Thus, the experimentally interesting quantity would not be a unique set of frequencies, but rather the *density of states*, an average of the eigenvalues over all the possible structures

$$D(\omega) = \left\langle (3N)^{-1} \sum_{\alpha=1}^{3N} \delta(\omega - \omega_\alpha) \right\rangle. \quad (2.4)$$

In the special case that we are dealing with a liquid, we have the additional problem that almost none of the liquid configurations will correspond to even local minima, much less to the global minimum. However, it is worth pointing out where the problems are and where they are not. The  $D$  matrix could still be calculated from Eq. (2.3) for each liquid configuration (each arrangement of the atoms) and a density of states derived by Boltzmann averaging the resulting eigenvalues over the configurations, as in Eq. (2.4). Hence this frequency spectrum remains perfectly well defined in a liquid. The question is just what does this spectrum mean?

It is, in fact, possible to consider these modes as representing the exact short-time dynamics in a precisely defined sense—which suggests that we ought to call them the *instantaneous normal modes*.<sup>25,26,29</sup> The reasoning goes as follows: At any instant (time  $t = 0$ ), the liquid will be at some configuration defined by the  $3N$ -dimensional vector of atomic coordinates  $\mathbf{R}_0$ . In general, there will not be anything noteworthy about this configuration, but we can nonetheless imagine expanding the potential about  $\mathbf{R}_0$  through harmonic order

$$V(\mathbf{R}) = V(\mathbf{R}_0) - \mathbf{F}(\mathbf{R}_0) \cdot (\mathbf{R} - \mathbf{R}_0) + \frac{1}{2}(\mathbf{R} - \mathbf{R}_0) \cdot \mathbf{d}(\mathbf{R}_0) \cdot (\mathbf{R} - \mathbf{R}_0), \quad (2.5)$$

where  $\mathbf{F}(\mathbf{R}_0)$  is the ( $3N$ -dimensional) force vector at  $\mathbf{R}_0$  and  $\mathbf{d}(\mathbf{R}_0)$  is the Hessian matrix of the potential [which, in turn, is closely related to  $\mathbf{D}(\mathbf{R}_0)$ , the dynamical matrix evaluated at  $\mathbf{R}_0$ ,

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

for a system of  $N$  identical atoms each of mass  $m$ .

Since the system is usually not at a potential minimum, the force term will rarely vanish, which means that the system will not be undergoing small oscillations. Thus our harmonic expansion will converge only when the magnitude of the vector  $(\mathbf{R} - \mathbf{R}_0)$  is small for some other reason. But, an interesting special case occurs when we interpret  $\mathbf{R}$  as the liquid configuration after the system has evolved some time  $t$  from the starting configuration  $\mathbf{R}_0$ . Clearly such an  $(\mathbf{R} - \mathbf{R}_0)$  will always be small for short enough times  $t$ . Therefore the normal modes arising from the diagonalization of  $\mathbf{D}(\mathbf{R}_0)$  will indeed be the correct short-time modes.

The frequency spectrum calculated in this way can be useful to the study of clusters in several capacities. For one thing, we can identify particular bulk and surface modes and we can single out modes that are clear precursors of sharp features in the bulk solid. Another interesting feature comes from the fact that some of the eigenvalues  $\omega_\alpha^2$  will be positive and others will be negative. That is, some of the frequencies will be real and others will be imaginary. Presumably, the way to think about the latter is to note that imaginary frequencies correspond to motion on an upside-down potential (normally associated with crossing a barrier or saddle point). The fraction of such modes should therefore be a measure of the extent of diffusive or fluidlike motion.<sup>25,26</sup>

A more direct indication of the fluidity of the cluster is actually available from this spectrum. To the extent that the expansion (2.5) is valid, we should be able to use it to find the time evolution of the liquid explicitly. Suppose we know the eigenvalues and eigenvectors of the dynamical matrix for any one configuration. Then straightforward matrix manipulations allow us to rewrite Eq. (2.5) as a sum over independent harmonic contributions

$$V(\mathbf{R}) = V(\mathbf{R}_0) + \sum_{\alpha=1}^{3N} \left[ - (f_\alpha/m^{1/2})q_\alpha + \frac{1}{2} \omega_\alpha^2 q_\alpha^2 \right], \quad (2.6)$$

where the  $q_\alpha$  are the  $3N$  normal coordinates (mass weighted) and the  $f_\alpha$  are the transformed forces. It is now a simple matter to solve Newton's laws for the time evolution of the

coordinates and velocities for each mode separately. As is usual for a harmonic oscillator, one will get linear combinations of  $\sin \omega_\alpha t$  and  $\cos \omega_\alpha t$  terms for all of the real frequency modes ( $\alpha = 1, \dots, n_{\text{real}}$ ). Similarly, if for the imaginary frequencies we define  $\omega_\gamma^2 = -\Omega_\gamma^2$ , then one will get linear combinations of  $\sinh \Omega_\gamma t$  and  $\cosh \Omega_\gamma t$  terms for all of the imaginary frequency modes ( $\gamma = 1, \dots, n_{\text{imag}}$ ).

Given this information, we can calculate the normalized velocity autocorrelation function

$$C(t) = \frac{\sum_{j=1}^N \langle \mathbf{v}_j \cdot \mathbf{v}_j(t) \rangle}{\sum_{j=1}^N \langle \mathbf{v}_j \cdot \mathbf{v}_j \rangle} = (3N)^{-1} (m/k_B T) \sum_{j=1}^N \langle \mathbf{v}_j \cdot \mathbf{v}_j(t) \rangle, \quad (2.7)$$

where  $\mathbf{v}_j(t)$  is the velocity of the  $j$ th atom at time  $t$  and  $\mathbf{v}_j \equiv \mathbf{v}_j(0)$  is the corresponding velocity at time zero.<sup>30</sup> Note that the average here is over all possible initial conditions of the classical trajectory. That is, it is over all  $\mathbf{R}_0$  and all the initial velocities. Since it can be shown that both the numerator and denominator can be expressed as a sum over the contributions from each normal mode

$$C(t) = \frac{\sum_{\alpha=1}^{3N} \langle v_\alpha v_\alpha(t) \rangle}{\sum_{\alpha=1}^{3N} \langle v_\alpha v_\alpha \rangle},$$

with  $v_\alpha = dq_\alpha/dt$ , the exact velocity autocorrelation function implied by Eq. (2.5) can be written

$$C(t) = (3N)^{-1} \left\langle \sum_{\alpha=1}^{n_{\text{real}}} \cos \omega_\alpha t + \sum_{\gamma=1}^{n_{\text{imag}}} \cosh \Omega_\gamma t \right\rangle. \quad (2.8)$$

The reader is referred to a previous paper for details.<sup>25</sup>

Ideally, we would like to be able to use the Green-Kubo relationship between the self-diffusion constant  $D$  and this velocity autocorrelation function to compute the amount of diffusion occurring in our clusters.<sup>31</sup>

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}_j \cdot \mathbf{v}_j(t) \rangle = (k_B T/m) \int_0^\infty dt C(t). \quad (2.9)$$

However, this formula relies heavily on knowing the behavior of  $C(t)$  at long times, something which our manifestly short-time dynamics cannot give us. In fact, our  $C(t)$  function will diverge at long times whenever there are imaginary frequency modes. Fortunately, we can take advantage of the fact that the short-time behavior predicted by Eq. (2.8) is exact. If we expand Eq. (2.8) in a Taylor series, the first three nonvanishing terms

$$C(t) = 1 - A_2 t^2 + A_4 t^4 + \dots, \\ A_2 = \frac{1}{2} (3N)^{-1} \left\langle \sum_{\alpha=1}^{n_{\text{real}}} \omega_\alpha^2 - \sum_{\gamma=1}^{n_{\text{imag}}} \Omega_\gamma^2 \right\rangle, \\ A_4 = \frac{1}{4!} (3N)^{-1} \left\langle \sum_{\alpha=1}^{n_{\text{real}}} \omega_\alpha^4 + \sum_{\gamma=1}^{n_{\text{imag}}} \Omega_\gamma^4 \right\rangle \quad (2.10)$$

can be shown to be exact by using standard sum rules for the spectra of random matrices. The coefficient of  $t^2$ , e.g., just

brings in the trace of the dynamical matrix—which, after dividing by  $3N$ , gives the average squared frequency

$$\omega_E^2 = (3N)^{-1} \left\langle \sum_{\alpha=1}^{n_{\text{real}}} \omega_{\alpha}^2 - \sum_{\gamma=1}^{n_{\text{imag}}} \Omega_{\gamma}^2 \right\rangle. \quad (2.11)$$

The square root of this average is conventionally called the *Einstein frequency*  $\omega_E$ , since  $m\omega_E^2$  is then the average force constant for the system.<sup>25</sup>

This information can be used to help us estimate the diffusion constant if we are willing to *assume* a form for the asymptotic decay of  $C(t)$ . The simplest such assumption would be to write<sup>32</sup>

$$C(t) = \exp(-A_2 t^2), \quad (2.12)$$

which would lead, with Eq. (2.9), to

$$\begin{aligned} D &= (k_B T/m) \frac{1}{2} (\pi/A_2)^{1/2} \\ &= (k_B T/m) (\omega_E)^{-1} (\pi/2)^{1/2}. \end{aligned}$$

This form for  $C(t)$  leads to respectable estimates for the diffusion constants of bulk liquids, but it fails to take into account the mildly oscillatory nature of  $C(t)$ . Even in liquids, there is a small negative region due to back scattering.<sup>33</sup> A somewhat better version, therefore, comes from writing<sup>34</sup>

$$C(t) = \text{sech } at \cos bt, \quad (2.13)$$

and determining the unknown coefficients  $a$  and  $b$  by the requirement that the Taylor series expansion of this  $C(t)$  match the exact one through order  $t^4$ . Equation (2.9) would then imply that

$$\begin{aligned} D &= (k_B T/m) \pi [2(c-1)A_2]^{-1/2} \\ &\quad \times \text{sech}\{(\pi/2)[(5-c)/(c-1)]^{1/2}\}, \\ c &= 6A_4/A_2^2. \end{aligned} \quad (2.14)$$

In dense Lennard-Jones liquids, at least, the results from Eq. (2.14) are within 5% of the diffusion constants derived by direct computer simulation of the mean-square displacement of atoms.<sup>34</sup> We should thus be able to use Eq. (2.14) with some measure of confidence in the liquid region to estimate the diffusion constants of our clusters from their frequency spectra.

There is actually yet another application of this development. Because its short-time behavior is exact, we expect that the instantaneous-normal-mode correlation function (2.8)—and any form fit to it—should reflect the true velocity autocorrelation function, at least until some time  $\tau$  that the fundamental harmonic expansion (2.5) breaks down. Presumably, once that time is reached, Eqs. (2.8), (2.12), and (2.13) should all begin to diverge from one another. Moreover, for times much longer than  $t = \tau$ , one would also expect to be able to see  $C(t)$  begin to grow unphysically due to the cosh  $\Omega t$  terms. We should therefore be able to figure out a time scale for the validity of the harmonic expansion simply by examining the different predictions of Eqs. (2.8), (2.12), and (2.13). Just such a comparison is shown in Fig. 1 for an  $\text{Ar}_{13}$  cluster.

The details of our determination of the necessary frequency spectrum via simulation will be given in the next

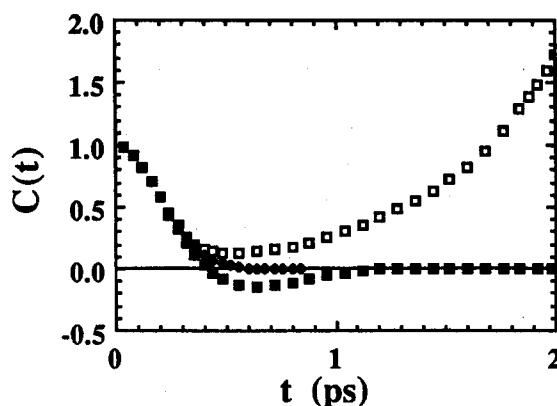


FIG. 1. The time dependence of the normalized velocity autocorrelation function calculated for a Lennard-Jones  $\text{Ar}_{13}$  cluster at 30 K. The three curves correspond to the complete instantaneous-normal-mode expression underlying the present work (open squares), and the simpler expressions given by Rice (solid diamonds; Ref. 32) and by Douglas (solid squares; Ref. 34).

section. Suffice it to say here that the averaged density of states from Eq. (2.4) is all that is needed in order to evaluate all three expressions. Precisely as one would have surmised from our discussion, the three formulas do lie virtually on top of one another until about 0.5 ps, at which time the normal-mode prediction starts to become unphysical. We are led, then, to a more concrete interpretation of the limitation of our harmonic expansion to “short” times. Under these conditions, it means times under half a picosecond.

Before concluding this section, we should emphasize that the general idea of calculating vibrational frequency distributions for nonrigid systems,<sup>35</sup> and for clusters in particular,<sup>8,14,16–19,36,37</sup> is not a completely new one. All of the previous work on clusters, however, has defined the distribution to be the Fourier transform of the velocity autocorrelation function. This transform technique will not, in general, produce a spectrum identical to ours, so it is worthwhile commenting on the relationship between the two formulations. To begin with, it is possible to show that both approaches correctly predict the phonon spectrum of a rigid solid at low temperature.<sup>38</sup> One way to see this fact is to observe that for a rigid solid, there are *only* small oscillations about the equilibrium positions, so that our velocity autocorrelation function (2.8) becomes the correct one even for long times. But, taking the Fourier transform of Eq. (2.8) gives precisely a sum of delta functions at the frequencies  $\omega_{\alpha}$ —exactly our result from Eq. (2.4)—so the two methods do give identical results in this limit.

When the system is heated somewhat, the answers will start to differ.<sup>39</sup> While deciding which approach is preferable may then depend on what phenomena one is trying to understand, it should be emphasized that the modes discussed here are the *exact* ones relevant to short-time dynamics. Of course, it might also be noted that the power spectrum of the velocity autocorrelation function has a statistical mechanical pedigree of its own. Not only is it rigorously true that this power spectrum evaluated at zero frequency must give the self-diffusion constant,<sup>14,18</sup> the whole spectrum, when calcu-

lated in this fashion, is a particular limit of the so-called dynamical structure factor. Hence this spectrum is, at least in principle, directly observable via an incoherent, long wavelength, scattering experiment<sup>31</sup>—meaning that, unlike the case with the instantaneous normal modes, one could imagine constructing an experimental observable out of the velocity autocorrelation function without making any assumptions about time scales, or equivalently, about the presence or absence of anharmonicity. Still, there are a number of practical advantages to using the instantaneous normal modes as a diagnostic tool. The velocity power spectrum contains no information about the average value or width of the imaginary peak, or, for that matter, any information about the Einstein frequency. Another point especially relevant to cluster work is that the instantaneous normal modes can be computed in any ensemble (and thus via either Monte Carlo or molecular dynamics), allowing us to make some interesting comparisons. The power spectrum, on the other hand, must be calculated in the microcanonical ensemble using molecular dynamics.<sup>40</sup>

Some basically analogous remarks are in order about our scheme for estimating the self-diffusion constant as well. The obvious way to compute an exact value for  $D$  is to do a molecular dynamics simulation and look at the mean-squared displacement of a tagged atom as a function of time.<sup>31</sup> If the motion is genuinely diffusive, at long times one should find a linear dependence on  $t$  with a slope of  $6D$ , but even though atomic displacements in clusters have long been studied, systematic diffusion constant calculations are rare.<sup>7</sup> One fundamental problem is that in any system of a finite size (such as a cluster), the displacement cannot continue to grow as  $t$ ; it has to be bounded—which means, formally, that  $D$  has to equal zero. Now, in practice there does seem to be an intermediate time range over which the time dependence is linear,<sup>14</sup> but there are no guarantees. The instantaneous normal mode estimate, of course, remains unambiguously defined under all circumstances and for all ensembles.

### III. COMPUTATIONAL SCHEME

Any actual calculation of the properties of a cluster or any other physical system requires the choice of a potential energy function. Previous studies of argon clusters for the most part have been based on pairwise additive Lennard-Jones potentials and so the majority of our calculations have been performed with this assumed potential. Specifically,

$$V = \sum_{i,j} u(r_{ij}),$$

$$(i > j)$$

$$u(r_{ij}) = 4\epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6],$$

where we have made the conventional choices for the well depth  $\epsilon$  ( $1.67 \times 10^{-14}$  erg) and for the length parameter  $\sigma$  ( $3.4 \times 10^{-8}$  cm).<sup>41</sup>

Although the qualitatively correct Lennard-Jones potential form has the virtues of being simple and convenient to use, it certainly is not the best available two-body potential for argon. Much better quantitative results for bulk properties of argon have been obtained by using the Aziz–Chen HFD-C potential<sup>42</sup>

$$u(r_{ij}) = \epsilon [Ae^{-ax}x^7 - (C_6x^{-6} + C_8x^{-8} + C_{10}x^{-10})F(x)],$$

$$F(x) = \begin{cases} \exp\{-[(D/x) - 1]^2\} & x < D \\ 1 & x \geq D, \end{cases}$$

$$x \equiv r_{ij}/r_m.$$

The complete list of argon parameters for this potential form are easily found in the literature,<sup>43</sup> but it is useful to note one of them in particular here. Specifically, the well depth  $\epsilon$  in the Aziz–Chen parametrization is equal to 143.224 K, as opposed to 120 K given by the conventional Lennard-Jones parametrization. We should expect, therefore, that the use of Lennard-Jones potentials will lead to a systematic underestimation of argon cluster binding energies and, perhaps, an increase in the facility of structural rearrangements.

We have not investigated the effects which the addition of  $n$ -body ( $n > 2$ ) terms might have in our calculations. Although two-body potentials such as the one by Aziz and Chen yield excellent values of bulk argon properties and thus account for the higher-order interactions at least in some average way, one cannot necessarily conclude that multi-body effects are negligible in small systems. In fact, there are a number of direct indications that such interactions must be included if the correct structures of small metal clusters are to be predicted.<sup>44</sup>

The calculation of cluster phonon spectra and diffusion constants via the approach described in the previous section requires that one generate a set of instantaneous system configurations. These configurations can be obtained in one of two ways, either by means of a molecular dynamics (MD) simulation, or, since the desired quantities do not exhibit an explicit time dependence, by means of a suitable Monte Carlo (MC) game. This latter approach has the potential of being the more desirable way of proceeding in that such methods often provide the only practical means of sampling the entire phase space available to the system. A well-recognized problem with using exact trajectories appears when the system dynamics exhibits a separation of time scales and it becomes difficult to obtain information concerning the long-time-scale dynamics without sacrificing an accurate description of the short-time-scale processes. Although there is a practical limit to the length of the trajectories run under these conditions, the Monte Carlo game may be extended arbitrarily in systems such as these until an equilibrium distribution of configurations has been generated. Since in the past some of the differences found in various studies of the rigid–nonrigid transition in argon clusters have been attributed by some workers to the use of trajectories which were too short,<sup>9,14,16</sup> we are sensitive to the need of an adequate averaging over *all* the phase space accessible to the system and therefore have chosen to base all our cluster phonon analyses on the results of MC calculations. We also note that an added advantage of the use of a MC approach is that Metropolis sampling techniques<sup>45</sup> can be equally applicable (although this fact appears to be poorly appreciated) to the construction of both canonical and microcanonical averages. Thus, since the two ensembles cannot in general be expected to yield the same results in a small system, we are in

a position to identify the consequences of both types of averaging without sacrificing the aforementioned advantages of MC calculations.

There are a number of good reviews of Metropolis MC methodology,<sup>46</sup> and so we will highlight only a few particular points here. Briefly, the method centers around the generation of a Markov chain of system states by means of a random walk in the space over which one desires to calculate averages. The key to the success of the method lies in the way in which trial steps in this random walk are either accepted or rejected by application of a rule involving the probability density characteristic of the ensemble. (The interested reader is referred to an especially lucid description of this process given by Brady, *et al.*)<sup>47</sup> In the vast majority of the applications of the Metropolis MC method, the ensemble of interest is the canonical ensemble, with the calculations involving only a Boltzmann weighting of system positions, but one may just as easily sample from a microcanonical ensemble and average both over positions and over momenta. Although isoergic MC calculations represent only a small fraction of our calculations, the relative unfamiliarity of most workers with this particular technique leads us to consider it in more detail here. Formally, in the isoergic case, one needs to choose a probability distribution which is a delta function  $P(\mathbf{r}, \mathbf{p}) = \delta[E - H(\mathbf{r}, \mathbf{p})]$ , but of course such a choice is impractical when used in calculations. Instead, one can make use of any of several prelimit expressions for the delta function, with the Lorentzian expressions used previously by Brady, *et al.*<sup>47</sup> and by one of us<sup>48</sup> being chosen for the present work. The probability of the system being in state  $i$  is therefore just

$$P_i(\mathbf{r}, \mathbf{p}) = \begin{cases} \frac{\epsilon}{\epsilon^2 + [\Delta E_i(\mathbf{r}, \mathbf{p})]^2} & |\Delta E| < E_s, \\ 0 & |\Delta E| \geq E_s, \end{cases}$$

where  $\Delta E_i$  is the difference in energy between the  $i$ th state and the desired total energy,  $E_s$  is the width of the energy shell (taken to be 10 K here), and  $\epsilon$  is a conveniently chosen small parameter (equal to 4 K in the present work following the suggestion of Brady, *et al.*)<sup>47</sup> Since the microcanonical probability distribution necessarily couples coordinates and momenta, both sets of dynamical variables must be "walked" in isoergic calculations. (In practice, it is convenient to take a step in the random walk which involves the  $\mathbf{r}$  and  $\mathbf{p}$  displacements of a pair of particles with their relative displacements being such that there is no center-of-mass motion of the system in the space-fixed coordinate frame.) Initial sets of variables consistent with the chosen system energy are easily obtained via the prescription given by Amar and Berry.<sup>15</sup> In this procedure, the positions are chosen by means of an isothermal Metropolis walk which continues until a configuration having a total potential energy falling on the energy shell as defined above has been located. The initial momenta are then set to zero, so that the total system energy is just the potential energy of the selected configuration. Isoergic equilibration steps are of course required prior to the generation of system configurations (involving both positions and momenta) in order that the system memory of the special starting conditions be lost.

Whether it be by sampling from a canonical or microcanonical ensemble, once a set of equilibrated cluster configurations has been generated, it is a simple matter given the chosen potential energy description to construct the Hessian matrix in mass-weighted Cartesian coordinates and to obtain the eigenvalues using a standard diagonalization algorithm. Three of these eigenvalues obtained for each configuration, corresponding to overall cluster center-of-mass motion, are zero. Since, however, the MC walks are not constrained so as to yield zero cluster angular momentum, the three cluster rotational degrees of freedom are not projected out from the vibrational degrees of freedom. We note that this fact points to a fundamental difference between our calculations and those previously reported,<sup>11,14-16</sup> which have involved a zero angular momentum constraint. Actually, we feel our calculations are more likely to reflect the true physical situation in clusters in that they do *not* presume a particular angular momentum value and they do not artificially ignore the role of vibration-rotation coupling in the equilibration process.<sup>49</sup>

Finally we note a couple of other details which enter into our computations. The first involves the nature of the boundary conditions in our problem. As a number of other workers have noted, a cluster having free boundary conditions (i.e., a cluster *in vacuo*) eventually will evaporate.<sup>14,50</sup> This problem becomes particularly acute in our studies at elevated temperatures (obviously the term elevated is a relative one—here we mean temperatures on the order of 35–40 K) when the MC walk has a higher probability of accessing regions of phase space corresponding to the dissociated cluster. But even at lower temperatures, this dissociative part of phase space is accessible. The perturbation of the system dynamics resulting from enforcing cluster binding by placing the system in some sort of reflecting cavity unfortunately can be nonnegligible, since this construction corresponds to an artificial pressurization of the system.<sup>12</sup> We have chosen to adopt a compromise procedure whereby the random walk steps are automatically rejected if the acceptance of the step would result in the total potential energy of any of the argon atoms dropping below 5% of the equilibrium diatomic well depth. Note that this prescription does not preclude a fissioning of the cluster, but in practice the splitting off of more than one argon atom at once is an improbable event except at the highest temperatures. The signature of fission at elevated temperatures is easily recognized, however, in that fission yields a very large increase in the system's potential energy. When we do see fissioning, we simply choose to declare that the system temperature is too high and we opt not to pursue further that particular temperature regime.

The second point deals with the method in which we estimate the error bars for our calculated quantities. Characteristically, we have included 200 individual cluster configurations (with 5000–15 000 MC steps between adjacent configurations) and have calculated standard deviations based on the constancy of the average values calculated from five groups of 40 configurations each. The frequency distributions obtained in this work are extremely broad and so large variations are seen among the individual configurations, but these variations become much smaller when the averages are



taken over blocks of configurations. While it is always desirable to include more configurations and thereby to improve the statistics further, our few trial calculations performed using more configurations have not produced results which differ significantly from those obtained using only 200 configurations. Obviously, this relatively small number of configurations would be woefully inadequate if we were not to allow for a large number of equilibration steps between configurations, since then the successive configurations would be highly correlated.

#### IV. RESULTS

##### A. Phonon spectra of argon clusters

We begin our survey of the results obtained by means of the instantaneous normal mode analysis with an examination of the calculated frequency spectra. In Fig. 2, one finds

spectra for the  $\text{Ar}_{13}$  cluster at three different temperatures derived from isothermal MC calculations using the Lennard-Jones potential function. (Note that for ease of presentation, the negatives of the absolute values of the imaginary frequencies are plotted on the same axes as the real frequencies.) Excluded from these plots are the three zero-frequency modes obtained at each cluster configuration corresponding to translation of the overall system center-of-mass. Since, however, our calculations have not included an imposition of the condition that the cluster angular momentum be zero, rotational modes are seen as well as modes deriving from a coupling of rotational and vibrational motion. That the rotations provide the primary contribution to the peaks observed at very low (real or imaginary) frequencies is easily confirmed by means of a calculation of the spectrum of  $\text{Ar}_2$ . The results of this calculation are displayed in Fig. 3 along with the analogous results from the  $\text{Ar}_{13}$  calculation as well as

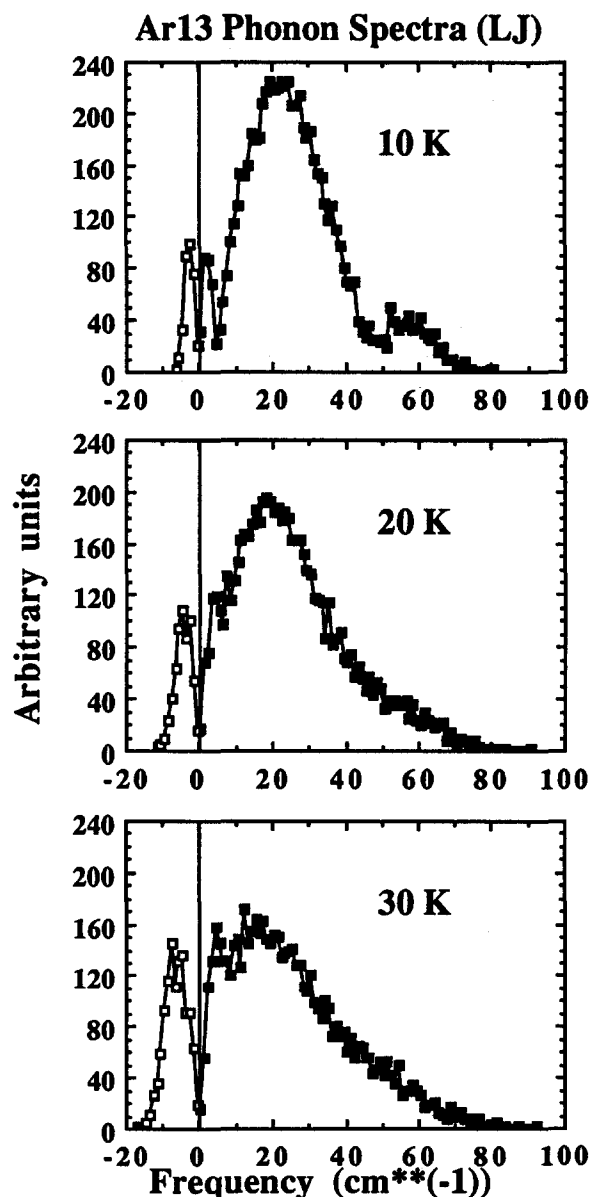


FIG. 2. Phonon spectra calculated at three different temperatures for a Lennard-Jones  $\text{Ar}_{13}$  cluster on the basis of 200 Monte Carlo isothermal configurations. Imaginary frequencies are plotted on the negative frequency axis.

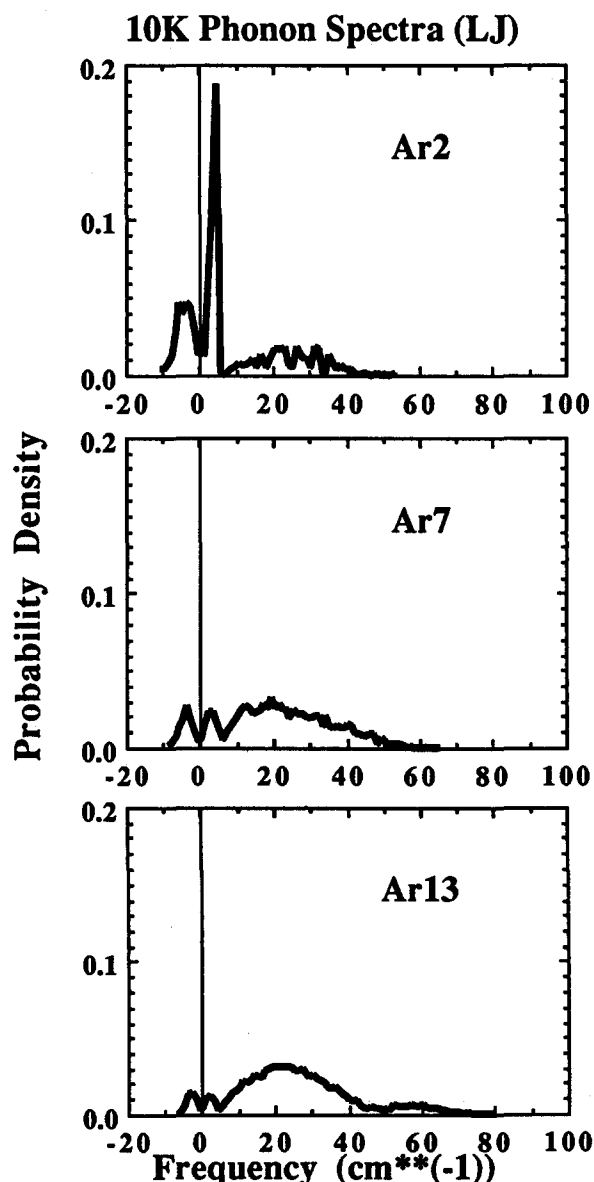


FIG. 3. Normalized phonon spectra calculated at 10 K for three different Lennard-Jones argon clusters.



those from a calculation involving  $\text{Ar}_7$ , about which more will be said later. In order to make a comparison among the three systems having differing numbers of degrees of freedom, these spectra have been normalized to unit area under the curves. A direct examination of the contributions to the prominent low-frequency peaks in  $\text{Ar}_2$  reveals that the constituent frequencies always occur in pairs for a given cluster configuration. Of course the dimer has at most a single vibrational mode, but possesses two degenerate rotational degrees of freedom, and so the assignment of the low-frequency peak to cluster rotational modes can be made unambiguously. This peak becomes less prominent as the number of atoms in the cluster (and hence the total number of degrees of freedom) increases and should vanish in the bulk limit.

The general change observed in the phonon spectrum when the cluster temperature is increased is a shift in the position of the peak in the real frequencies towards lower frequencies and a diminution of the magnitude of that peak. Concurrently, one finds an increase in the size, both in height and width, of the peak corresponding to the imaginary frequencies. Physically, these characteristic changes signal a "softening" of the vibrational modes of the cluster as the temperature rises and an increased probability that the cluster will sample regions of space which describe isomerizations. The transition from quite rigid structures at low temperatures to more "fluid" ones at the higher temperatures, which is suggested by this series of phonon spectra, is quite consistent with the overall dynamical picture reported previously by Berry and co-workers,<sup>14,16,17</sup> by Andersen,<sup>11</sup> and by others.<sup>9</sup> Notably absent in our calculated spectra is any evidence of a dramatic alteration as we pass through a special "melting" temperature. The two lower temperatures considered here are below the transition region reported by Berry, *et al.*,<sup>16</sup> while the higher temperature (30 K) lies in the middle of this transition region, but we nonetheless find the spectral changes to be a fairly smooth function of temperature and to extend over the entire range of temperatures considered.

There is another feature deserving mention in the  $\text{Ar}_{13}$  phonon spectra, specifically the discrete high-frequency peak observed in the results at 10 K. This peak is located at about  $60 \text{ cm}^{-1}$ , just the frequency at which one observes longitudinal phonon modes in solid argon.<sup>38,51</sup> Thus at low temperatures, the  $\text{Ar}_{13}$  cluster displays some of the characteristics of the bulk solid phase. Presumably this behavior stems from the fact that for the 13-atom cluster, the central atom of the cluster is effectively located in the same environment where it would be found in the crystal. Note that as the temperature is increased, the ensuing disordering of the cluster is characterized by a disappearance of the peak.

Of course, the calculated cluster phonon spectrum depends directly upon the choice adopted for the argon-argon potential energy function. As we noted above, the Lennard-Jones potential, while very widely used, is inferior to the more complex Aziz-Chen potential<sup>42,43</sup> in the prediction of bulk argon properties. We therefore have recomputed the phonon spectra for  $\text{Ar}_{13}$  using the better potential description, the results of that recalculation being given in Fig. 4. A quick comparison of the two sets of spectra reveals a qualita-

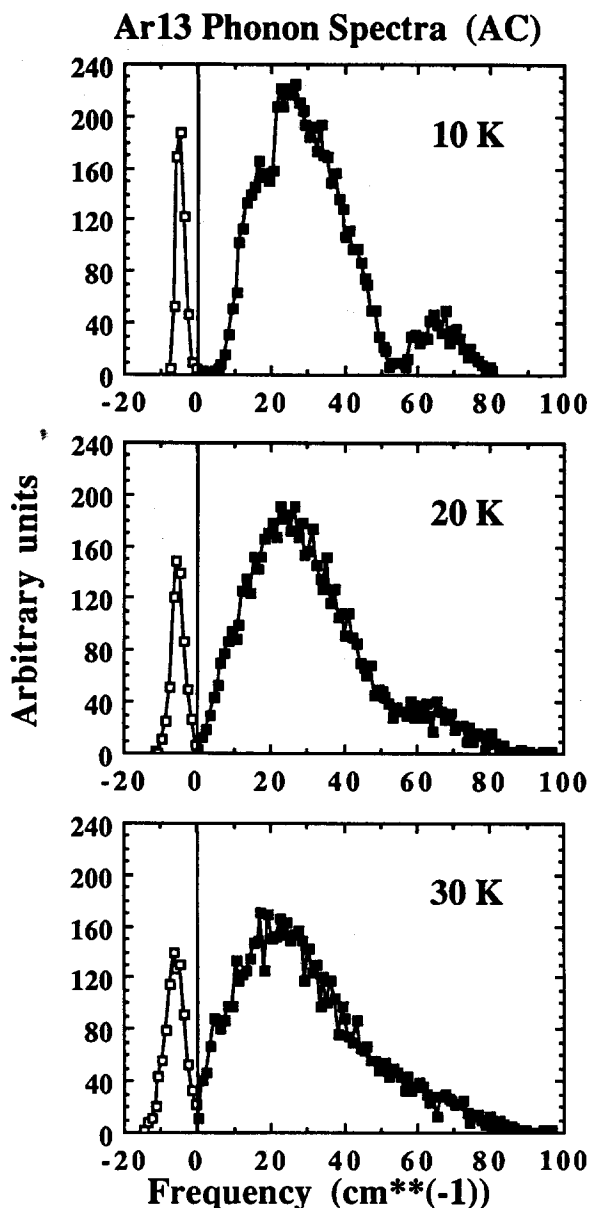


FIG. 4. Phonon spectra as in Fig. 2, except that they were calculated using the Aziz-Chen potential (Ref. 42).

tive agreement sufficient to give us confidence that our results are not dominated by artifacts arising from the potential energy description, but there still are a few differences which are deserving of note. First, the high-frequency secondary maximum corresponding to solid argon longitudinal modes is more pronounced and persists to higher temperatures when the Aziz-Chen potential description involving deeper two-body potential wells is used. Second, the low-frequency peak deriving from cluster rotational modes appears to have shifted to higher frequencies, merging with the low-frequency edge of the principal peak. This effect may derive from an enhanced coupling here of the rotational modes with the low-frequency cluster vibrations. And finally, the distribution of imaginary frequencies is slightly different in the two cases. Although at 10 K both potential de-

scriptions yield between 4% and 5% imaginary frequencies, this percentage rises more rapidly with temperature in the Lennard-Jones case, where one finds 16% of the frequencies (plus or minus about 1%) to be imaginary in contrast to the 12% found when the Aziz-Chen potential is used. This difference again can be attributed to the higher binding energies predicted by the Aziz-Chen potential and, consequently, the higher local potential barriers to isomerization.

It is interesting to compare the phonon spectra for  $\text{Ar}_{13}$  with those for a smaller Lennard-Jones cluster  $\text{Ar}_7$  at the same three temperatures (see Fig. 5). Once more, we find the general trend that the peak in the real frequencies diminishes and shifts towards lower frequencies as the temperature is increased. Although a few modes are found to move to higher frequencies, a larger number shift into the region of the low-frequency rotational spike or become imaginary. Here we no longer observe a high-frequency maximum in the

spectrum at low temperatures reminiscent of bulk longitudinal phonon modes. This result is not all that surprising when one recognizes that for such a small cluster, all the atoms are likely to lie on the cluster surface and thus none of the atoms are found in a bulklike environment.

While there is a solidlike signature in the low-temperature  $\text{Ar}_{13}$  results, the basic shapes of all the phonon spectra are very similar to those reported by Seeley and Keyes<sup>26</sup> for Lennard-Jones liquids using the same instantaneous normal mode analysis. In addition, the temperature dependence of their liquid spectra compares well with that which we have observed for small clusters. This similarity itself suggests a couple of generalizations about the dynamics of these small systems. First, even though well-defined minimum energy structures for the cluster may exist, the fact that we find nonzero fractions of imaginary frequencies indicates that the system may not be characterized adequately in terms of these minima alone. Therefore the relevant distribution of structures (including those *not* defined by the criterion that the forces vanish) may not be described well by a model which is based solely on inherent structures. The obvious consequence of this observation is that valuable insight into the nature of cluster dynamics can be overlooked in a molecular dynamics study which relies on periodic quenching of trajectories in order to probe cluster structure.<sup>11,15,18</sup> Second, the striking similarity between the temperature dependence of the phonon spectra of a cluster and a liquid would tend to argue against there being a sharp dynamical transition (analogous to a bulk phase transition) as one passes through a particular temperature. Instead, one would expect to find a fairly smooth dynamical progression as the system overcomes a nearly continuous distribution of local potential maxima with an increase in temperature.

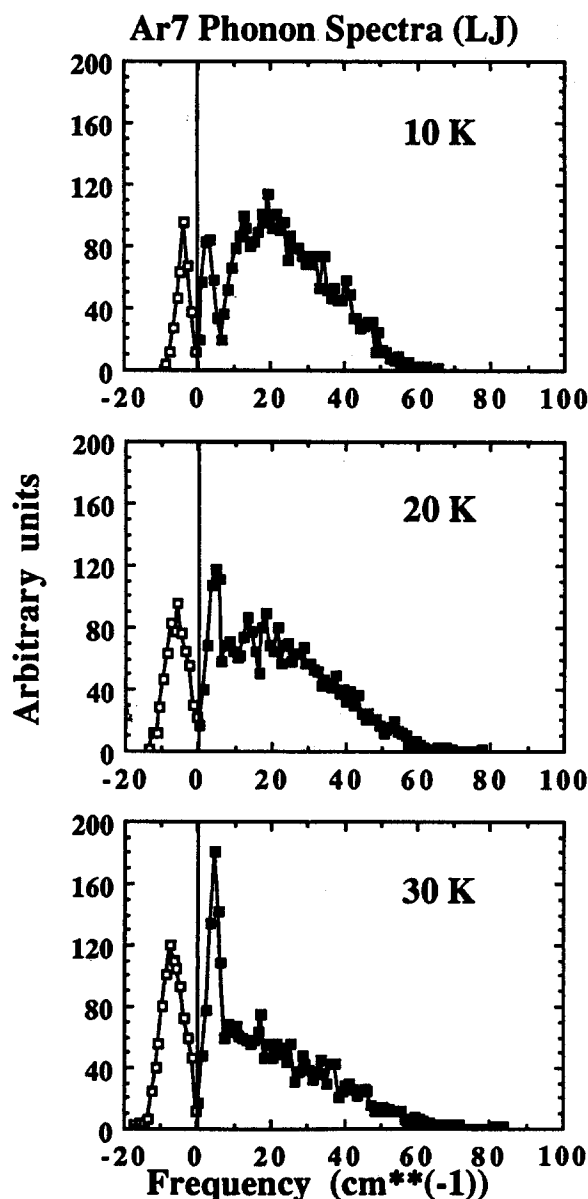


FIG. 5. Phonon spectra as in Fig. 2, but for a Lennard-Jones  $\text{Ar}_7$  cluster.

## B. Analysis of the frequencies

We now turn to a more detailed look at the frequency distributions obtained from the instantaneous normal mode analysis with the specific goal of characterizing any dynamical transition which may be occurring in these small cluster systems. First, however, it is useful to consider the temperature dependence of the average potential energy of the cluster configurations, the results for  $\text{Ar}_{13}$  (Lennard-Jones potential) being displayed in Fig. 6. The curve of the average potential energy exhibits a break in curvature at a temperature of 27.5–30 K and thus compares well with the energy vs temperature plot previously reported by Honeycutt and Andersen<sup>11</sup> (the break in their curve appears at about 28 K) as well as with the binding energy vs temperature plot given earlier by Etters and Kaelberer,<sup>10</sup> also obtained via isothermal MC calculations. In addition, the position of the curvature break agrees with the melting temperature reported by Berry and co-workers.<sup>14,16</sup> This curve was found to be of considerable practical importance during the calculations as a monitor of the completeness of the equilibration of the MC walk at a given temperature. We observed that as more equilibration steps were included in the walk and as longer intervals were inserted between the configurations actually used

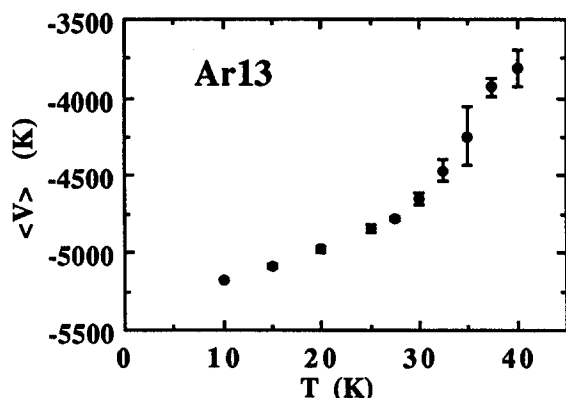


FIG. 6. The temperature dependence of the average potential energy of a Lennard-Jones  $\text{Ar}_{13}$  cluster. The error bars denote one standard deviation in the data. In this and all subsequent figures, 200 Monte Carlo configurations were used in the averaging process (five blocks of 40 configurations).

in the normal mode analysis, the calculated average potential energies tended to converge towards the points depicted in Fig. 6. When a point was calculated which lay off this curve, we immediately became suspicious of the degree of equilibration in that particular calculation and recalculated the point using more MC steps. In all cases, we found that the extended equilibration procedure brought that value of the average potential into line with the others.

Of course, the discontinuity in the curvature of the plot (though not in the average values themselves) is significant in that it suggests the presence of energy thresholds in the cluster isomerization process. Below this critical temperature, one may indeed find that isomerizations occur, but the clusters tend to oscillate about highly symmetric, low-energy structures. Above this temperature, the system has sufficient energy to surmount the local potential barriers and to move into regions of coordinate space characterized by more disordered structures. So this plot indeed suggests that some sort of dynamical transition is occurring in the  $\text{Ar}_{13}$  clusters, even though it does not provide much insight into the exact nature of the transition.

One of the most straightforward and simplest ways of characterizing the temperature dependence of the cluster phonon spectra is in terms of the partitioning of the vibrational degrees of freedom between real and imaginary modes. In the top panel of Fig. 7, we give the percentage of the 36 nonzero  $\text{Ar}_{13}$  modes which are imaginary over the temperature range 10–40 K. For the most part, the plot is a smooth curve having a slope which increases with  $T$ , the only deviation from this behavior being seen at the highest temperature. It is hard to know quite what to make of this deviation, though since also at 40 K the probability of evaporation of one or more argon atoms from the cluster is high. (This enhanced probability is manifested as an increased number of MC configurations which meet the criterion for reflection mentioned in Sec. III.) Notably absent in this graph is any indication of a discontinuity which might be expected if the system undergoes an abrupt transition between rigid and fluid structures. The observed behavior is not inconsistent, however, with a more gradual, essentially

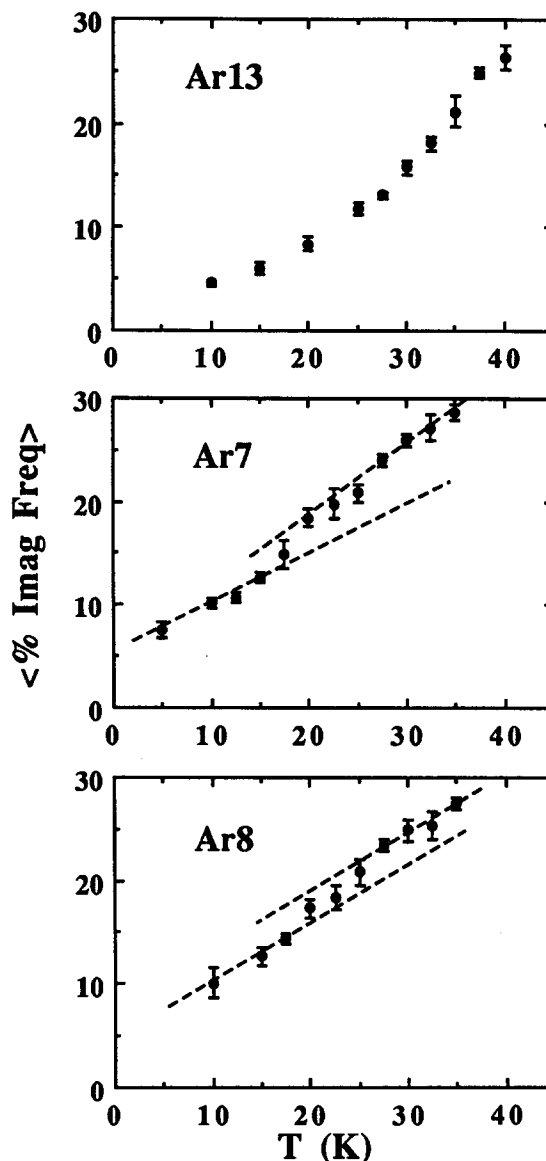


FIG. 7. The average percentage of the calculated  $3N - 3$  nonzero instantaneous normal mode frequencies which are imaginary for three different Lennard-Jones argon clusters. The dashed lines are meant only to guide the eye and do not represent a fit to the data.

continuous series of transitions involving a large number of intermediate structures.

Far more dramatic is the behavior seen in the analogous results obtained for  $\text{Ar}_7$ , which are displayed in the central panel of Fig. 7. Here the transition between dynamical regimes in which the average percentages of imaginary frequencies have distinctly different temperature dependence is unmistakable. The temperature range over which this transition occurs is, roughly, 15–20 K, which agrees well with the “melting range” of 16–20 K reported by Amar and Berry<sup>15</sup> for this system and which is consistent with the melting temperature of 15.7 K extracted from the data of Etters and Kaelberer.<sup>10</sup> It is also particularly interesting to compare these results with those for  $\text{Ar}_8$  (lower panel of Fig. 7), a cluster which Berry and co-workers<sup>17</sup> have found to show a different sort of transition behavior (one lacking a bimodal

distribution of kinetic energies). Our results suggest that the dynamical similarities between the  $\text{Ar}_7$  and  $\text{Ar}_8$  clusters actually may be greater than previously thought, in that the average percentage of imaginary frequencies in both cases is found to have a sigmoidal temperature dependence. In the  $\text{Ar}_8$  results, however, we find that the slope of the curve is essentially the same prior and subsequent to the transition region (here roughly 17–25 K). That we observe a transition regime for  $\text{Ar}_8$  really should not be viewed as all that surprising; if the transition is thought of as a progression through an ever increasing number of structural isomers, then there is no reason why such behavior should be unique to  $\text{Ar}_7$ , even though 7 is at least a weak “magic number.” Perhaps the facts that the transition region is spread over a wider temperature range in  $\text{Ar}_8$  and that the temperature dependence of the percentage of imaginary frequencies before and after this transition is nearly the same have helped make the detection of a transition region in this cluster difficult.

Given these findings for  $\text{Ar}_7$  and  $\text{Ar}_8$ , we are led to re-evaluate the results obtained in the large 13-atom cluster. The change in the slope of the curve of the top panel of Fig. 7 can be interpreted to signal a transition regime which is markedly larger than the one seen for the smaller clusters. Here the high temperature turnover is not reached by the time that evaporation of atoms from the surface of the cluster has become significant. (We may be seeing the onset of this turnover at 40 K, the highest temperature considered, but the results calculated for temperatures at the upper limit of practical cluster stability are necessarily somewhat uncertain.) The transition region reported by Davis, *et al.*<sup>16</sup> on the basis of isothermal MD calculations (using the Nosé method<sup>52</sup>) extends over the region 26–37 K; we consider this result to be in reasonably good agreement with the present work.

In Fig. 8, we give the average real and imaginary frequencies calculated from the 200 MC configurations generated at each temperature. The general trends here are that while the average imaginary frequency increases monotonically with temperature, approaching an asymptotic value, the average real frequency exhibits a distinct plateau behavior at intermediate temperatures. Note in particular that the end of this plateau behavior occurs at the same temperature (30 K) where one finds the discontinuity in the slope of the  $\langle V \rangle$  vs  $T$  curve (Fig. 6). The temperature dependence of the average imaginary frequency is fairly easy to understand; as the system temperature is increased (and thus the average energy of the cluster is increased), it becomes possible for higher local barriers to isomerization to be surmounted, with these barriers being associated with larger imaginary frequencies. The slope of the plot of the average imaginary frequency vs temperature does not remain constant, though, since in the more fluid (i.e., disordered) cluster, the majority of barriers to free motion already have been overcome. More difficult to understand is the plateau behavior seen in the plot of the average real frequency. The basic trend here, namely the overall decrease with temperature, clearly reflects the average softening of the vibrational modes of the cluster, in part due to the increased probability of isomerization, but also as a result of an overall thermal expansion of the cluster. However, there appears to be a region in which

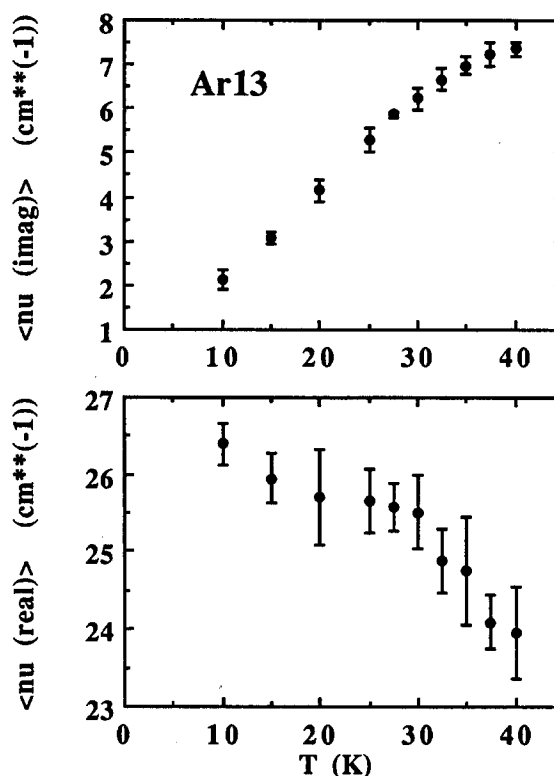


FIG. 8. The average values of the imaginary and real instantaneous normal mode frequencies calculated for a Lennard-Jones  $\text{Ar}_{13}$  cluster.

little change is seen in the higher-frequency cluster vibrations, which dominate the calculated real frequency average, even though the lower-frequency vibrations are varying (with some of these modes becoming isomerization paths associated with imaginary frequencies). Such behavior is in accord with a model in which even though the local bonding environment is not changing appreciably (and hence the short-time-scale motion consisting of the oscillations of atoms about their local equilibrium positions is only slightly perturbed), there is an increase in the amount of long-time-scale (long-wavelength) motion characteristic of isomerizations. One therefore should be wary of viewing the transition merely as ever increasing amplitudes for displacement of a system away from a single, well-defined minimum energy configuration. Our findings are more consistent with a picture of isomerizations occurring among a number of locally similar, but globally distinct intermediate configurations and are very much in the spirit of the work of Honeycutt and Andersen,<sup>11</sup> who have suggested that transitions should not be viewed solely in terms of jumps between a rigid and a fluid structure.

Finally, we give the average Einstein frequencies determined for the  $\text{Ar}_{13}$  Lennard-Jones cluster (Fig. 9). Note the unmistakable discontinuity in the slope of the data between 27.5 and 30 K. Recall from the discussion of Sec. II that here we are seeing the temperature dependence, essentially, of the root mean square of the mode frequency (i.e., save for some constants, the square root of the average nonzero eigenvalue

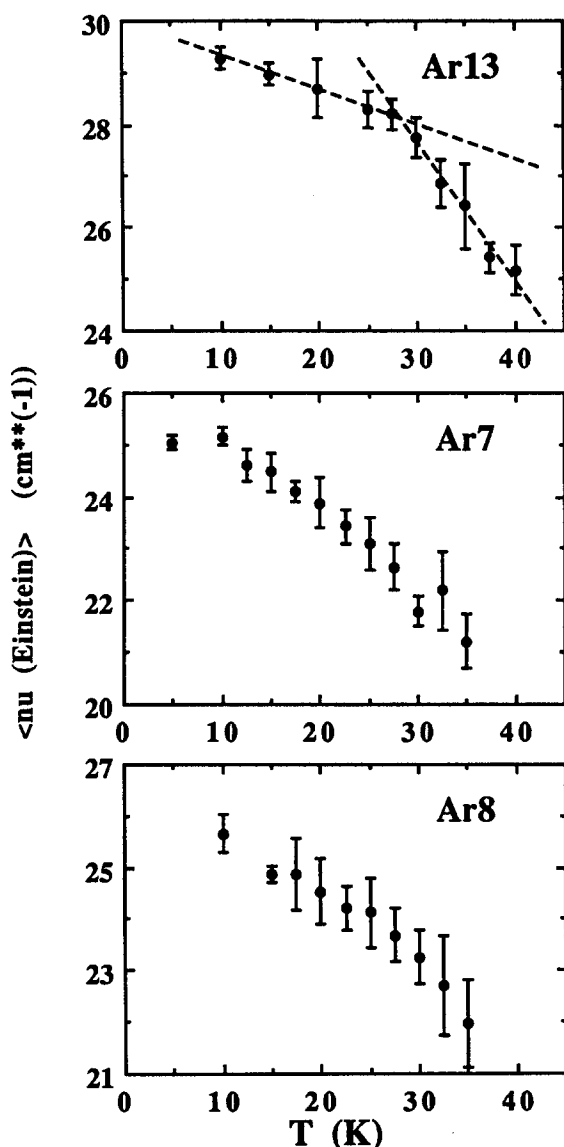


FIG. 9. The average values of the Einstein frequency of a Lennard-Jones  $\text{Ar}_{13}$  cluster. The dashed lines are meant only to guide the eye and do not represent a fit to the data.

of the dynamical (Hessian) matrix). Thus it is not surprising that the behavior of the average Einstein frequency roughly tracks that of the average real frequency, since in  $\text{Ar}_{13}$  the real frequencies represent 70% or more of the total number and the magnitudes of the imaginary frequencies are relatively small.

Since they are simply measures of the average force constant, the values of the Einstein frequency also provide a simple quantitative measure of the general trends seen in the temperature dependences of the photon spectra (Figs. 2 and 5). Consequently, we can obtain a useful overview of the cluster size-dependent aspects of the phonon spectra via a comparison of the Einstein frequencies calculated for  $\text{Ar}_{13}$ ,  $\text{Ar}_8$ , and  $\text{Ar}_7$  (again see Fig. 9). We find that for both of the smaller clusters, any discontinuity in the slope of  $\tilde{\nu}_E (= \omega_E/2\pi c)$  vs  $T$  is much less pronounced than it is for the larger cluster. In particular, we again note only minor

differences in the average gross vibrational structure of the seven- and eight-atom clusters, in distinct contrast to the significant dynamical differences that have been reported previously for these systems.

### C. Cluster self-diffusion constants

As we have mentioned above, the calculation of instantaneous normal modes affords a straightforward means of estimating self-diffusion constants for atoms in small clusters.<sup>7</sup> A summary of these calculations is given in Fig. 10 for the three clusters considered in this work. First note that the order of magnitude of the diffusion constants is what one might expect for a condensed phase, although a direct comparison with the corresponding bulk values is problematic given the dependence of  $D$  on the density of the bulk and the fact that volume and thus density are ill-defined quantities for cluster atoms. All of the data show a change in slope, although the change is less marked for  $\text{Ar}_8$ , with the point at

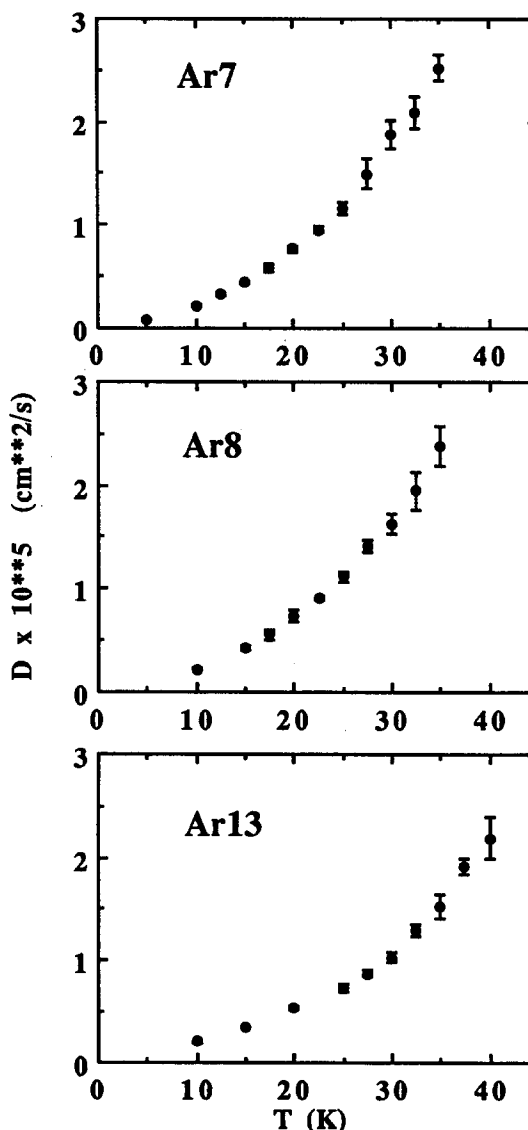


FIG. 10. The estimated self-diffusion constants for three Lennard-Jones argon clusters in the canonical ensemble.

which the change occurs moving to higher  $T$  as the cluster size is increased ( $\approx 22$ – $25$  K for  $\text{Ar}_7$  and  $\text{Ar}_8$ ,  $\approx 30$ – $32$  K for  $\text{Ar}_{13}$ ). It is interesting that at the points where the slopes of  $D$  vs  $T$  change, all the clusters are characterized by a self-diffusion constant value of roughly  $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . This behavior is noteworthy in light of the picture afforded by the simple Lindemann model, which correlates melting in any system with a 10% relative fluctuation in the distance of a particle from its nearest neighbors.<sup>14,16</sup> We have intentionally avoided any reference to nearest-neighbor separations in our analysis of cluster dynamics— $D$  itself is a global variable which is not limited to the measurement of near-neighbor bond displacements—but it is clear that increases in the average interparticle separation eventually will lead to increases in the self-diffusion constant. It therefore seems entirely reasonable that a critical separation criterion for defining fluidity be intimately linked with some minimum diffusion constant for clusters exhibiting liquidlike dynamics. However, we believe the diffusion analysis is an especially attractive approach to the description of cluster melting inasmuch as while  $D$  is equally well defined for the solid and liquid phases, the notion of nearest neighbors fails for liquids (although not for their underlying inherent structures). We also should note that the particular critical value suggested here ( $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) represents a sensible demarcation between diffusion constants for bulk liquids and solids.

#### D. Self-diffusion constants in a microcanonical ensemble

It is well known that in general averages obtained within a canonical ensemble are equal to those calculated for a microcanonical ensemble only in the limit of an infinitely large number of particles. Since the small argon clusters considered here clearly do not fulfill this condition for the equivalence of the two approaches, separate calculations are required in order to obtain the isothermal and isoergic quantities. This point has been recognized by others who have carried out MD calculations on these systems, although in some cases workers have found the results using the two ensembles to be qualitatively the same.<sup>14,16</sup> We have chosen to select just one of our clusters for a separate isoergic MC study in order to obtain some sort of indication of what sorts of differences should be expected in the dynamics computed using the constant temperature and constant energy approaches.

Figure 11 (top panel) contains the results of these isoergic calculations on an  $\text{Ar}_7$  Lennard-Jones cluster, with the diffusion constant being plotted vs the system energy in units of the Lennard-Jones two-body well depth  $\epsilon$ .  $D$  is found to be a nearly linear function of  $E$  over the range of energies considered here (roughly analogous to the temperature range 10–20 K), with there being perhaps a slight increase in the slope of the data at energies greater than  $-13\epsilon$ . A recent calculation by Beck<sup>53</sup> of diffusion constants of argon clusters based on an MD evaluation of the velocity autocorrelation function also yields a linear dependence, and so it seems that there is a real difference between the energy dependence observed in isoergic calculations and the temperature depend-

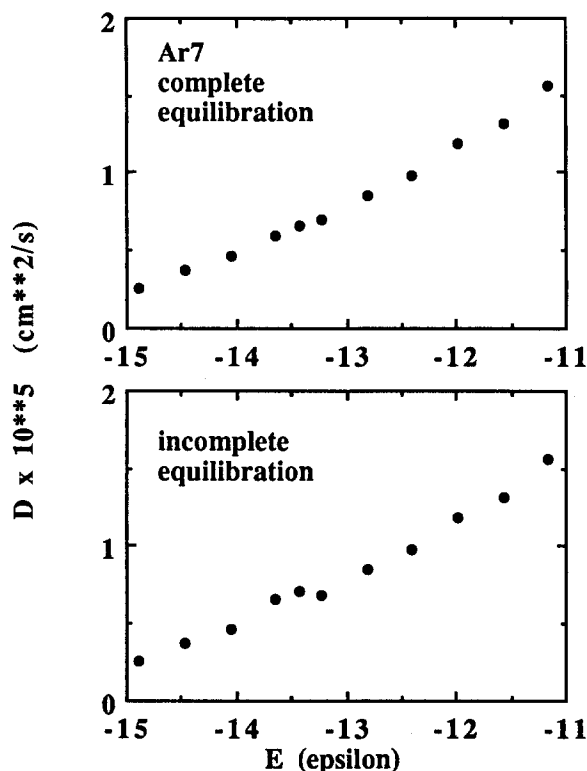


FIG. 11. The estimated self-diffusion constant for a Lennard-Jones  $\text{Ar}_7$  cluster calculated in the microcanonical ensemble. The lower panel represents a lesser degree of cluster equilibration over the middle of the energy range.

ence observed in isothermal calculations. The absence of a clear signature of a dynamical transition in these results is particularly significant in light of the seemingly obvious markers reported by Berry and co-workers<sup>14,16</sup> in their MD calculations.

These isoergic calculations also provide a convenient means for demonstrating the dependence of the final results on the adequacy of the phase space sampling procedure which one has adopted. In practice, this criterion means either that MD trajectories are sufficiently long or that MC walks include a sufficient number of steps that the cluster configurations are indeed representative of a well-equilibrated system. The lower panel of Fig. 11 shows results analogous to those of the panel above it, but with half as many steps included in the Monte Carlo walk. Note that a more irregular energy dependence is found at intermediate energies when the system equilibrium is incomplete. Actually, our calculations have indicated that it is only at these intermediate energies that  $D$  is particularly sensitive to the degree of equilibration. Such inadequate equilibration procedures very likely were responsible for the peculiar van der Waals loop structure reported previously by Briant and Burton<sup>9</sup> (described, ironically, in a paper which stressed the need for careful equilibration protocols) and may be at the root of much of the confusion presently concerning argon cluster dynamics.

## V. CONCLUDING REMARKS

The focus of this paper has been an examination of dynamical transitions in small argon clusters via an analysis of their instantaneous normal modes, which reflect the exact short-time dynamics of these systems. Such an approach is particularly attractive in that unlike strategies founded on an enumeration of minimum energy structures, it is equally applicable to both microscopic and macroscopic systems. It also is quite versatile in that it makes no special assumptions about the nature of the forces acting in the system and so can be applied to systems in which many-body forces are significant. Finally, our approach carries with it the distinct computational advantage that the instantaneous normal modes may be computed using either MC or MD techniques and within any desired ensemble.

The overall picture of the dynamical transitions occurring in the isothermal  $\text{Ar}_n$  ( $n = 13, 7, 8$ ) clusters considered in our study is not one which emphasizes the importance of jumps between configurations characterized as either solid-like or liquidlike, but rather one which stresses that any such transitions constitute a series of isomerizations. These isomerizations reflect an average increase in the long-wavelength motion of the cluster in the absence of a significant alteration of the local oscillations of the individual argon atoms. The results also suggest that the systems are often quite far from their minimum energy configurations (inherent structures); even at low temperatures, there is a nonzero probability that isomerizations will be observed. Although the development of such a model has relied on a variety of measures of the dynamics, we have found the calculation of the self-diffusion constant, the average Einstein frequency, and the percentage of imaginary frequencies to be particularly helpful. The reader is reminded, however, that this picture represents in fact a description of the average behavior of a collection of clusters and not actually of the detailed time dependence of any particular cluster. Such is the general characteristic of results obtained from MC calculations, of course, but then it is also the characteristic of current experimental results with which these calculations might be compared.

Given the substantial body of work concerning both the average and the detailed dynamics of these small argon clusters, it is appropriate to ask what directions should be pursued in further studies of clusters. First, there is a need for investigations of inherently different sorts of clusters, e.g., those which are more tightly bound or those in which strong directional bonding effects are likely to be found, but second, it is important that theoretical studies of dynamical transitions begin to emphasize experimental observables. Presumably this emphasis means establishing a link between the transitions and spectroscopic signatures, since surely it is spectroscopy which in the future will provide the greatest increases in the body of information about these systems. As just one example of these investigations, we note the recent work of Hahn and Whetten,<sup>6</sup> who have produced  $\text{Ar}_n$ -benzene clusters and have observed changes in spectral line shapes as the number of argon atoms is varied. We currently are applying the instantaneous normal mode analysis to just

this system in order to see if we can understand the dynamical details underlying the experimental findings.

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