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The quantum mechanics of clusters: The low-temperature equilibrium and dynamical behavior of rare-gas systems

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We consider in the present paper the quantum-mechanical effects on the equilibrium and dynamical behavior of low-temperature rare-gas clusters. Using a combination of ground-state and finite-temperature Monte Carlo methods, we examine the properties of small (2–7 particles) neon clusters. We find that the magnitude of the equilibrium quantum-mechanical effects in these systems is significant. The present studies also suggest that the low-temperature dynamics of these rare-gas systems is appreciably nonclassical.

I. INTRODUCTION

Studies of the equilibrium and dynamical properties of clusters constitute a significant and increasingly active area of current research. Interesting because of their rich and varied phenomenology, clusters are also of substantial practical importance. They are intimately involved, for example, in such important processes as nucleation, thin-film growth, and catalysis. Beyond their intrinsic merit, however, clusters also serve as convenient prototype systems in the analysis of other, more complex condensed phase and interfacial problems. Both conceptually and practically, clusters bridge the gap between finite and bulk systems. Cluster investigations also provide an important common ground for few- and many-body techniques and serve to clarify the transition between finite and extended system behavior.

As reviewed in detail elsewhere,¹ a variety of experimental techniques can and have been utilized in cluster investigations. This rich experimental base provides the necessary foundation for the sustained development of this topic.

From an applications viewpoint, cluster systems are convenient testbeds for the development of numerical methods. In smaller clusters the microscopic force laws are typically better characterized than the corresponding force laws for general bulk systems. Comparisons of theoretical predictions and experimental data in such systems are thus, in principle, less clouded by uncertainties in the fundamental interactions than would generally be the case. Moreover, the intermediate scale of clusters permits a variety of theoretical techniques to be brought to bear on a common problem thus facilitating the testing and development of what are hopefully more generally useful methods.

The basic theoretical tools available for the study of the equilibrium and dynamical properties of clusters were, until recently, classical in nature. Monte Carlo and molecular dynamics methods have been used to probe the equilibrium and dynamical properties of such systems. Beyond the assumption of classical behavior, such methods are free of further

untestable numerical approximations. The rare-gas thermodynamic studies of Lee, Barker, and Abraham² and the molecular dynamics studies of Berry *et al.*³ are examples of such classical investigations.

For many problems classical mechanical studies are appropriate and yield physically relevant predictions. For other problems, however, quantum-mechanical effects are significant, casting doubt on the adequacy of purely classical approaches. There now exist a broad class of both zero- and finite-temperature equilibrium quantum-mechanical methods that are applicable to many-body systems in general and to cluster studies in particular. A number of applications of these methods to cluster problems have been reported. Such applications have included numerical path-integral techniques;⁴ variational,⁵ diffusion, and Green's-function Monte Carlo methods;⁶ and basis set methods.⁷

The present work is a preliminary step toward the general study of the quantum-mechanical effects on the *dynamics* of many-body systems. The particular physical context of the present study is the low-temperature dynamics of small rare-gas clusters. Our work is motivated in part by the recent investigations of Beck *et al.*⁸ who examined the quantum-mechanical effects on "melting" in small neon systems. That study found that the effects of quantum mechanics on melting were significant. In particular, the large zero-point fluctuations found in small neon clusters raise questions concerning the qualitative character of these low-temperature systems and the extent to which their dynamical behavior can be adequately described by classical methods.

Both finite- and zero-temperature methods are employed in the present work. These methods are summarized briefly in Sec. II. In this brief review we concentrate principally on finite temperature and diffusion Monte Carlo approaches and refer the interested reader to recent work⁹ that focuses purely on the cluster ground-state properties for a more complete description of the variational Monte Carlo method. Section III describes the application of these methods to neon and argon clusters and draws a number of conclusions concerning the nature of the low-temperature cluster dynamics. The conclusions of the present work are summarized in Sec. IV.

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II. METHODS

In the present study we will be concerned with single-component rare-gas clusters. We will assume that the interactions in such systems are described by a simple superposition of pair potentials, with the pair interaction taken here to be the familiar Lennard-Jones potential,

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2.1)$$

In this expression ϵ and σ denote the usual well depth and size parameters. In the present studies these parameters were taken to be (35.6 K, 2.749 Å) for neon and (119.4 K, 3.405 Å) for argon, respectively. This empirical force law is adequate for our current purposes and, moreover, its use will also allow us to draw on the results of a number of previous, Lennard-Jones based investigations. We emphasize, however, that the theoretical methods used in the present study are neither restricted to pairwise additive interactions in general nor to Lennard-Jones forms in particular. Although not the principal focus, we will also briefly consider helium clusters in the present work. For those applications, the helium-helium interaction was assumed to be of the Aziz form.¹⁰

The characteristics of the stable isomers predicted by minima in the cluster interaction potential as well as the nature of their interconnecting transition states are valuable in the characterization of the cluster dynamics. Such information is available for many of the smaller clusters.¹¹ Depicted in Fig. 1, for example, are the four stable isomers and the associated potential energy minima for a seven atom Lennard-Jones cluster. Associated transition-state geometries

and energies that connect these stable potential minima have been discussed recently by Wales and Berry.¹¹

Knowledge of the relative populations of these stable structures as a function of temperature offers valuable insight into the nature of the cluster dynamics.¹² Such relative populations can be obtained, for example, by quench studies based on randomly chosen equilibrium configurations.¹³ In such an approach each configuration is assigned a label corresponding to the particular "parent" structure found by a steepest descents potential-energy quench that starts at the configuration in question. The temperature dependence of the resulting quench populations is useful *both classically and quantum mechanically* in the characterization of the cluster dynamics.

Although not the principal focus of the present work, equilibrium Monte Carlo cluster studies provide sufficient information to approximate the rate parameters associated with the interconversion between the various stable cluster structures. For classical systems, established Monte Carlo transition-state methods are available for this purpose and are discussed in detail elsewhere.¹⁴ Analogous quantum-mechanical tools based on centroid path integral methods described in the work by Gillan¹⁵ and in that by Voth, Chandler, and Miller.¹⁶

In the present work we will be interested in the properties of finite clusters whose microscopic force laws are of the type described earlier. Since we are particularly interested in possible quantum mechanical effects, we will make use of direct comparisons between the predictions of classical and quantum-mechanical methods. We summarize these methods briefly and refer the interested reader to the published literature for more complete descriptions of the methods involved.

Classical mechanical methods have been applied to the study of the equilibrium and dynamical behavior of clusters by a number of investigators. These methods, as well as a number of recent applications, are reviewed by Berry *et al.*³ Once the microscopic force law is specified, Monte Carlo molecular dynamics and related methods produce estimates of the equilibrium and dynamical behavior free of untestable approximations beyond the assumption of classical behavior. These methods have been used, for example, to study cluster structure and to explore the magnitude of finite-size effects. They have also been used to study cluster precursors of familiar bulk phenomena such as melting and diffusion.¹⁷ More recently, nonlinear methods have been used to characterize the onset of irregular and chaotic behavior in the dynamics of these rare-gas clusters.¹⁸

In recent years, practical quantum-mechanical methods for the study of both zero and finite-temperature many-body systems have been developed. The finite-temperature techniques, in principle, contain the zero temperature results as a special limiting case. Although important advances have been made that extend the practical limits of these finite-temperature approaches to rather low temperatures,¹⁹ it is still generally useful to have available efficient, specialized techniques designed specifically to study quantum-mechanical ground-state problems.

One simple, but effective zero-temperature method is

Ne-7 Isomers

FIG. 1. Shown are the four stable structures for a classical seven-atom Lennard-Jones cluster. The energies (in units of the Lennard-Jones well depth) are shown with each structure.

the variational Monte Carlo technique.²⁰ In this approach Monte Carlo methods are used to evaluate the variational estimate of the total energy corresponding to some specified trial wave function. The expectation value of the Hamiltonian over this trial wave function provides an upper bound to the quantum-mechanical ground-state energy. This bounding property makes it possible to “optimize” the trial function by demanding that the associated energy be minimized with respect to any adjustable parameters present in the wave function. Since the integrals in the variational Monte Carlo method are estimated by statistical rather than analytical methods, the form of the trial function can be chosen on the basis of physical suitability rather than mathematical convenience. Recent applications of these variational methods to cluster problems as well as practical extensions to deal with excited states have been reported by Whaley *et al.*^{5,21} We utilize traditional variational methods in the present work to obtain estimates of the ground-state energies and wave functions for rare-gas clusters of various sizes. The wave functions used in the present study are described in detail by Rick *et al.*⁹ Generically, the variational forms used in the present work are of the form of a product of pair functions. In the case of helium and neon, the pair functions are of the type utilized by Whaley *et al.*⁵ with some modifications to introduce multiple length scales in the case of neon. More elaborate “shadow” trial functions^{9,22,23} are also used. For the argon clusters, the wave functions are designed to reflect more nearly the structure of the classical system.

Although the variational method described above is frequently quite useful, it is often desirable to utilize numerical methods that are arbitrarily refinable. One such method is the diffusion Monte Carlo (DMC) technique.²⁴ This method exploits the isomorphism between the time-dependent Schrödinger equation (written in imaginary time) and the diffusion equation. Statistical methods designed for the treatment of diffusion problems can thus be invoked to “solve” the original Schrödinger equation. The essence of these DMC methods can be seen by considering the Schrödinger equation for a particle of mass μ moving one-dimensional potential $V(x)$. The “time”-dependent equation in imaginary time ($\tau = it/\hbar$) becomes

$$\frac{\partial \psi}{\partial \tau} = \frac{\hbar^2}{2\mu} \frac{d^2 \psi}{dx^2} - [V(x) - E] \psi, \quad (2.2)$$

where the constant E has been subtracted from the potential for convenience. Disregarding its physical origin for the moment, Eq. (2.2) describes the “diffusion” of particles whose diffusion constant is $\hbar^2/2\mu$ in the presence of particle sources and sinks. The strength of these sources and sinks are governed by the second term on the right-hand side of Eq. (2.2), $[V(x) - E]\psi$. As discussed by Ceperley and Alder,²⁵ the solution of Eq. (2.2) is dominated for large values of τ by the lowest energy solution to the Schrödinger equation. The typical strategy for obtaining the ground-state wave function and properties from Eq. (2.2) is thus to devise a statistical procedure in which the “birth,” “diffusion,” and “death” processes are suitably modeled and examine the solution in the large τ limit. The details of these DMC methods, a complete description of the technical issues involved, and

numerous examples are discussed by Ceperley and Alder.²⁵ We briefly summarize certain technical issues specific to the present applications in the Appendix. Although not utilized in the present work, Green’s-function Monte Carlo methods²⁶ are also broadly applicable to the calculation of ground-state properties of many-body quantum-mechanical systems.

In the present work DMC methods are utilized to obtain what are effectively numerically exact estimates of the ground-state properties of various quantum-mechanical clusters. We have found these independent estimates of the ground-state properties to be valuable, limiting checks of the results of more general, finite-temperature methods. The present DMC applications utilize one feature that merits brief discussion and validation. As noted earlier, the birth and death processes in Eq. (2.2) are governed by the term $[V(x) - E]\psi$. If the potential is unbounded from below (such as would be the case for a Coulomb interaction), this term can lead to an infinite birth rate. This practical difficulty is typically avoided through the use of “importance sampling” methods in which Eq. (2.2) is used to derive a modified diffusion equation for the product of a trial wave function and its exact counterpart. In the resulting modified diffusion equation, the birth and death processes are governed by the difference between the “local energy” of the trial wave function and the constant E . This quantity is typically smaller than the corresponding term in Eq. (2.2) and thus the fluctuations in the population induced by the birth and death processes in the modified diffusion equation tend to be smaller than those in Eq. (2.2). The importance sampling results are formally independent of the choice of the trial functions. In the present applications, however, the qualitative nature of the ground state is an issue of primary interest. We have chosen, therefore, to use Eq. (2.2) *directly* to avoid any possibility of introducing a bias concerning the nature of the ground state through the choice of a trial wave function. We note in this regard that the Lennard–Jones interactions are bounded from below, and thus the infinite growth in the direct Monte Carlo approach is not an issue in the present work. As will be discussed in Sec. III, we have confirmed the reliability of this direct DMC approach for a variety of nontrivial cluster problems.

In addition to the ground-state methods described earlier, we have utilized numerical path-integral methods to examine the finite-temperature quantum-mechanical properties of the various rare-gas systems under investigation. The details of the Fourier path-integral techniques used here and their application to cluster problems are described elsewhere.^{4,27} The essential feature of such numerical path-integral approaches is that they express equilibrium properties of the quantum-mechanical problem as classical-like averages in an enlarged configuration space. That is, the quantum-mechanical averages emerge as higher-dimensional analogs of the original classical problem.²⁸ Once formulated in this manner, the same numerical Monte Carlo methods that were utilized to solve the original classical problem can be used to solve its quantum-mechanical analog. Since the numerical methods involved are relatively insensitive to dimensionality, the introduction of the additional degrees of free-

dom necessary to account properly for the quantum-mechanical features of the problem poses no special difficulties. Nonetheless, it is generally worthwhile as a practical manner to minimize the number of these auxiliary degrees of freedom. To this end we have used partial averaging methods to accelerate numerical convergence in the present work.²⁹ In the partial averaging approach the contributions of very short length-scale fluctuations to the path-integral results are approximated using low-order cumulant methods. The threshold for the use of cumulant methods is adjustable. In its most primitive form where *all* quantum-mechanical fluctuations are approximated, the partial averaging approach essentially reduces to the Feynman–Hibbs effective potential method. Unlike that approximation, however, the partial averaging method can be systematically refined. We note in passing that the partial averaging method has proved particularly useful recently in the treatment of the polaron problem.³⁰

As one last technical point, except for the studies involving helium, exchange effects appear to play a relatively minor role for the systems in the present investigation. Consequently, all path-integral calculations in the present work have been performed assuming Boltzmann statistics.

III. RESULTS AND DISCUSSION

We begin our study of the quantum-mechanical effects in the neon clusters with a simple order-of-magnitude estimate. Approximating the Lennard–Jones potential by a quadratic form whose frequency is chosen to match the curvature of the Lennard–Jones interaction near its potential minimum, an elementary harmonic treatment predicts a value of -0.4925ϵ for the ground-state energy of Ne_2 dimer. That the zero-point energy represents roughly a 50% modification of the classical bond strength suggests at the outset that quantum-mechanical effects are likely to be significant for the ground-state energetics of these systems. Moreover, at this relatively high energy the system will be probing regions of the potential energy outside the harmonic region thus making appreciable anharmonic effects also likely.

The above suggestions concerning the anharmonic, quantum-mechanical nature of the neon clusters are confirmed by direct diffusion Monte Carlo calculations. DMC calculations predict, for example, that the exact ground-state energy in Ne_2 is $-0.5667 \pm 0.0003\epsilon$, a value that is appreciably above the classical value. We note that anharmonic effects lower the ground-state energy by approximately 15% relative to the simple harmonic estimate discussed earlier. This direct DMC result for the neon dimer agrees well with the value of -0.5669ϵ obtained independently from a numerical integration of the relevant one-dimensional radial Schrödinger equation.

We find similar quantum-mechanical results for the neon trimer. Consideration of the trimer system is useful in that the various DMC and path-integral results obtained can be verified independently by other methods. Furthermore, the wave functions for this system are relatively easy to visualize and provide important insights into the extent of quantum mechanical delocalization.

Table I lists the ground-state energies of the neon and

TABLE I. Total energies (in units of ϵ) for the Lennard–Jones model of the Ne_3 and Ar_3 clusters computed by direct diffusion Monte Carlo (DMC), by discrete variable representation (DVR) methods and by variational Monte Carlo (VMC) techniques. The statistical uncertainties in the DMC results are indicated in parentheses.

Cluster	DMC	DVR	VMC
Ne_3	$-1.7174(5)$	-1.7178	-1.7046
Ar_3	$-2.5532(4)$	-2.5535	-2.5374

argon trimers computed by diffusion Monte Carlo methods and by the discrete variable representation (DVR) approach described recently by Leitner *et al.*⁷ The generally excellent agreement of the independently obtained results again suggests that the direct DMC method is reliable. A detailed discussion of the discrete variable results for the various rare-gas trimers is presented elsewhere.⁷ We note here that the ground-state energy of the neon trimer is appreciably above the classical ground-state energy of -3ϵ . In fact, this energy even lies above the minimum classical energy of the linear trimer (-2.031ϵ). A classical three-atom neon system with a total energy equal to the quantum-mechanical ground-state energy would therefore have sufficient energy to permit the “isomerization” of two equivalent triangular structures via a linear transition state. This situation is in contrast to the case of Ar_3 whose ground-state quantum-mechanical energy (-2.56ϵ) is below the classical threshold for isomerization.

Also displayed in Table I are the results of variational Monte Carlo calculations for the neon and argon trimers. These variational calculations are readily extended to larger rare-gas clusters and a number of such calculations have been reported. The results in Table I employed trial wave functions described in detail by Rick *et al.*⁹ These variational estimates are in reasonable agreement with the results obtained by the two other methods. Using the same type of trial function that was utilized for the neon and argon systems, we have also examined the ground state of the helium trimer. For this system we have utilized the Aziz potential¹⁰ rather than the Lennard–Jones form for the helium–helium interactions. The present variational Monte Carlo helium trimer wave function yields an estimate of $-0.0109 \pm 0.0001\epsilon$ for the helium trimer energy. This is in good agreement with the estimate of Pandharipande *et al.*,³¹ who obtained a value -0.0107ϵ for the helium trimer using Green’s-function Monte Carlo methods. As is evident from its very large zero-point energy, the quantum-mechanical effects for the helium trimer are substantial.

Of central interest in the present discussion is the degree of localization in the ground-state wave functions. Intuitively, we would anticipate that the quantum-mechanical effects in helium would be large and that the ground-state wave function of the helium trimer would be extensively delocalized. Conversely, we would expect that the wave function for the larger rare-gas trimer systems such as argon and beyond would be effectively localized in the vicinity of the classical ground-state structures. These limiting expectations

are confirmed in Fig. 2. These plots display the Ψ_1 wave functions of Ref. 9. The coordinates in Fig. 2 are the usual Jacobi coordinates (r, R, ϕ) , where R is the distance between two atoms, r is the distance between the center of mass of those two atoms and a third, and ϕ is the angle between unit vectors along r and R . We see in Fig. 2(a) that the ground-state helium trimer wave function is *extensively delocalized* and that there is appreciable amplitude in the vicinity of both the triangular and linear helium configurations. From Table I we see that the energy of the ground state of the argon trimer lies below the classical "isomerization" threshold, the energy of the linear trimer system. It is thus not surprising that the corresponding ground-state wave function for the argon system [Fig. 2(b)] is *strongly localized* in the vicinity of the classical (triangular) ground-state geometry, with essentially no amplitude in the linear trimer region.

Following the aforementioned discussion, we might anticipate that the extent of localization in the neon trimer is intermediate in character, lying somewhere between that of helium and argon. That the ground-state neon energy is above the classical isomerization threshold might suggest that the neon wave function would, in fact, be delocalized. We see in Fig. 2(c), however, that the neon ground-state wave function is *strongly localized* in the vicinity of the classical structure with relatively little amplitude in the vicinity of the linear configuration. This example and related results presented below for the seven-atom neon cluster makes it clear that we must exercise caution when deciding questions of localization and delocalization. In particular, it is inappropriate to decide this issue by simply comparing the total energy with classical isomerization thresholds.

The relative magnitudes of the quantum-mechanical ef-

FIG. 2. Shown are contour plots of the variational wave functions described in Ref. 9 for three atom rare-gas systems. Plots are for He_3 [Fig. 2(a)], Ar_3 [Fig. 2(b)], and Ne_3 [Fig. 2(c)] wave functions. Coordinates are the usual Jacobi coordinates (c.f. Fig. 2(b)) with $\phi = 90^\circ$. The two relevant configurations are the equilateral triangle ($R = 2r/\sqrt{3}$) and the collinear geometry ($r = 0$).

fects on the ground-state energies of larger clusters are similar to those found in the two- and three-atom systems. Figure 3 presents the DMC estimates of the ground-state energies for neon clusters ranging from two to seven particles. For comparison, we also present in Fig. 3 harmonic approximations to the various ground-state energies. We see from Fig. 3 that these systems, like the neon dimer, are characterized by appreciable, anharmonic quantum-mechanical effects.

With increasing temperature, the quantum-mechanical system begins to probe successively higher lying excited states. The interplay of these states is at the heart of the system's quantum dynamics. For that reason we now turn our attention to an examination of the behavior of our clusters at finite temperatures. Figure 4 displays the average cluster energies of 3–5 atom neon clusters as a function of temperature computed using Fourier path integral methods. The agreement between the limiting behavior of the low-temperature, distinguishable particle path-integral results and the separately computed, DMC Bose ground-state results suggests that the effects of particle statistics on the ground-state energies are minimal in these small neon clusters. For comparison, we also present in Fig. 4 the DMC and harmonic estimates of the ground-state energies of the various clusters. Total energies in the path-integral calculations were obtained using direct temperature differentiation of the partition function (T method) in conjunction with gradient partial averaging techniques. The improvement in the rate of convergence of the path-integral calculations provided by this partial averaging procedure is significant, as demonstrated in Table II. We note in passing that although the total energies produced by path-integral calculations are

FIG. 3. Energies of neon clusters as a function of the number of cluster atoms (N). Energies shown are in units of the Lennard-Jones well depth and correspond to the classical mechanical ground states (solid circles), diffusion Monte Carlo estimates of the quantum-mechanical ground states (open circles), and approximate quantum-mechanical results based on simple harmonic estimates of the zero-point energy (crosses).

FIG. 4. Energies of the Lennard-Jones model of 3–5 atom neon clusters as a function of temperature. Energies are in units of the Lennard-Jones well depth. Shown are the Fourier path integral Monte Carlo estimates (solid circles), the corresponding diffusion Monte Carlo estimates of the ground-state energies (solid line), and harmonic estimates of the ground-state energy (dashed line).

guaranteed to converge to the exact results as the number of Fourier coefficients is increased, the results are not guaranteed to converge to from a particular direction.

Using the path-integral and DMC methods discussed earlier, we have examined the energetics of larger neon systems. The path-integral and DMC energies obtained using the interaction potential described in Sec. II for Ne_7 are displayed in Fig. 5. For comparison, we also show in Fig. 5 the classical Monte Carlo energies as well as the known various thresholds for isomerization reported by Wales and

TABLE II. Total energies for the Lennard-Jones model of the Ne_7 cluster computed with and without partial averaging (PA) for various numbers of Fourier coefficients (k_{max}) at a temperature of 2 K. Energies are in units of the Lennard-Jones well depth. Estimates of the statistical uncertainties in the various results are shown in parentheses. Results shown are computed using the “ T method” (see text).

k_{max}	PA	no PA
2	− 9.26(2)	− 13.99(3)
4	− 9.49(2)	− 12.97(2)
8	− 9.62(2)	− 11.84(2)
16	− 9.68(2)	− 10.99(2)
32	− 9.64(4)	− 10.28(5)

FIG. 5. Energies of the Lennard-Jones model of the seven-atom neon cluster as a function of temperature. Energies are in units of the Lennard-Jones well depth. Shown are the Fourier path integral Monte Carlo estimates (solid circles), the corresponding classical estimates (open circles connected by a solid line), the diffusion Monte Carlo estimate of the ground-state energy (solid line), and the classical mechanical estimates of the energies of the transition states that interconnect the stable structures shown in Fig. 1 reported in Ref. 11.

Berry.¹¹ Several things are evident from Fig. 5. We focus the discussion first on the classical results. From Refs. 3 and 8 we know that the seven-atom *classical* Lennard-Jones system undergoes a rapid transition from a topologically ordered to disordered system in the temperature range of $k_B T/\epsilon = 0.10$ to 0.15 , a range that corresponds to 3.6 – 5.3 K for neon. From Fig. 5 we can see that this is the temperature range in which the system's energy classically begins to exceed the known rearrangement thresholds. With increasing energy the system's structure becomes more and more fluctuational, first exploring the anharmonic region in the vicinity of its lowest energy structure, and ultimately probing regions corresponding to successively higher lying isomers.

The temperature dependence of the classical cluster rearrangements can be made more explicit by the use of quench techniques.¹³ Shown in Fig. 6 are the fractions of configurations selected randomly from a Boltzmann distribution at a given temperature that quench to the four stable, seven-atom structures. We see from these results that at lower temperatures only configurations in the vicinity of the lowest energy isomer play a significant role. With increasing temperature, however, configurations that quench to non-ground-state configurations emerge, a signature of the onset

FIG. 6. Distribution of quench results performed on seven-atom classical neon clusters as a function of temperature. The four curves correspond to the four stable isomers in Fig. 1 whose energies are (in Lennard-Jones units) — 16.505 (open diamonds), — 15.935 (solid diamonds), — 15.593 (open circles), and — 15.553 (solid circles). Between one and ten thousand quenches were performed at each temperature on configurations selected randomly from a Boltzmann distribution via Monte Carlo methods.

of appreciable cluster isomerization. As will be emphasized again below, the strong temperature dependence of the classical quench populations provide us with evidence of the activated nature of the associated rearrangement dynamics. As discussed previously, rate parameters for the rearrangement kinetics could, in fact, be obtained for the rearrangements using Monte Carlo transition-state-theory methods.¹⁴

The increasing fluctuational character of the classical cluster in this temperature range is also reflected in other system quantities. For example, it can also be seen in the self-diffusion constants shown in Fig. 7. As discussed elsewhere,³ the mean-square displacements in finite systems often display a linear time dependence over a range of intermediate times. This linear dependence can be used to define "diffusion constants" in these finite systems. Here these diffusion constants were computed using a hybrid Monte Carlo-molecular dynamics approach in which a reasonable number (typically 1000) of cluster initial configurations were chosen randomly via the usual Metropolis procedure from a canonical ensemble at the desired temperature. Particles in these initial configurations were assigned momenta, also selected randomly from a Boltzmann distribution,³² and the resulting phase-space configurations were then propagated forward temporally using standard molecular dynamics techniques. Detailed discussions of the diffusion in these systems and discussions of other possible approaches for its study have been described recently by Adams and Stratt³³ and by Beck and Marchioro.³⁴

FIG. 7. Shown are values of the self-diffusion constant as a function of temperature for a seven-atom neon cluster. The solid circles are the results of the Monte Carlo-molecular dynamics calculations described in the text. The solid line, intended principally as a visual reference, is a cubic fit to the data.

We now turn our attention to the quantum-mechanical results in Fig. 5. The most striking thing evident in those results is that the ground-state energy in Ne_7 is already well *above* the relevant classical rearrangement thresholds. That is, a classical Ne_7 system with the same total energy content as the quantum-mechanical ground state has energetically allowed pathways available to it that connect the regions of its potential-energy surface that quench to all of the various stable isomers. As was the case with the neon trimer discussed earlier, however, a simple comparison of the system's total quantum-mechanical energy to its various classical rearrangement thresholds is not the relevant test for localization. In the present case, for example, we find the ground state of the Ne_7 system to be localized in the vicinity of the classical structure. This localization is evident in Fig. 8(a) and is in contrast to the situation with the He_7 system depicted in Fig. 8(b). The explanation of this localization is that in a many-dimensional system, there may exist degrees of freedom that are effectively uncoupled from the "reaction coordinate" involved in the isomerization process. Consequently, the zero-point energy in these "background" degrees of freedom is unavailable to the isomerization dynamics. As described elsewhere,^{9,35} it is thus more appropriate to describe the rearrangement dynamics in terms of a "vibrationally adiabatic" model rather than the simple classical picture. We close by noting the excellent agreement in Fig. 5 between the path-integral results at low temperatures and the DMC ground-state energy.

As with the classical results, the temperature dependence of the quench population derived from an equilibrium quantum-mechanical distribution offers insight into the cluster dynamics. To this end Fig. 9 compares the isomer distributions resulting from quenches of the equilibrium classical and quantum-mechanical distributions for Ne_7 as functions of temperature. Although slightly different in de-

FIG. 8. Contour plots of the variational Ne_7 [Fig. 8(a)] and He_7 wave functions [Fig. 8(b)] of Ref. 9. Coordinates are those described in detail in Appendix 1 of Ref. 9. The coordinates involved represent an overall scale factor (s) and an isomerization coordinate (r_{45}). This isomerization coordinate connects a pentagonal bipyramid structure [$r_{45}/s = \sin(3\pi/10)$] and a capped octahedral structure ($r_{45}/s = 1$) via a saddle ($r_{45}/s = \frac{1}{2}$). We see the Ne_7 function is localized near the classical minimum-energy structure (pentagonal bipyramid) while no such localization is evident in the He_7 wave function.

tail, both the quenches from the classical and quantum-mechanical results display a qualitatively similar temperature dependence. In particular, both results indicate that the rearrangement rates are strongly temperature dependent. We also note that the population of the lowest-energy isomer approaches 100% in the quantum-mechanical calculations,

FIG. 9. A comparison of classical and quantum-mechanical quench results for seven-atom neon clusters. Notation is that of Fig. 6. Quantum-mechanical results are connected by solid lines and the corresponding classical results are connected by dashed lines.

an indication of a localized ground state. We confirmed this localization by performing similar quench studies on the high quality Ne_7 ground-state wave function reported in Ref. 9. Quenches based on that shadow wave function indicate that approximately 99.95% of the configuration space density is associated with the classical ground-state isomer, in agreement with the aforementioned results.

We can see additional evidence of the activated character of the seven-atom cluster rearrangement dynamics for neon in Fig. 10. There we have displayed the results of quench studies performed on configurations for Ne_7 selected randomly from a quantum-mechanical distribution at 4 K. Although configurations in the vicinity of the lowest-energy isomer predominate, at this temperature the system accesses configurations corresponding to all stable structures. Transitions between these stable structures are clearly evident in Fig. 10. As the temperature is reduced, however, such transitions become less common. Furthermore, at lower temperatures configurations artificially started in the quench vicinity of the higher-energy structures have a tendency to cascade toward the lowest-energy structure. Such a cascade is illustrated in Fig. 11 for a temperature of 2 K. We see there that at this relatively low temperature, the clusters, having found their way to the vicinity of the lowest-energy structure, effectively never visit other minima in the potential energy.

IV. SUMMARY AND CONCLUSIONS

The present work has considered the equilibrium and dynamical behavior of neon and argon clusters at low temperature. These issues have been probed using a combination

FIG. 10. Shown are quench results for seven-atom, quantum-mechanical neon clusters. In these calculations a path-integral Monte Carlo sequence of configurations is generated at the specified temperature (4 K) and the resulting configurations are quenched. The three panels corresponding to different initial cluster geometries, here taken to be the configurations of the higher lying classical isomers (c.f. Fig. 1). The panels show the energies (in units of the Lennard-Jones well depth) of the final quenched configurations after a specified number of path-integral Monte Carlo sweeps. Quenches are performed after every 10 sweeps. The results indicate that at this temperature the system makes frequent transitions between the various stable classical isomers.

of zero- and finite-temperature Monte Carlo methods. Although not as dramatic as in the case of helium, we find the magnitude of the quantum-mechanical effects on the equilibrium properties of small (2–7 atom) neon and argon clus-

FIG. 11. As in Fig. 10 with $T = 2$ K. In each case the cluster tends to cascade to a geometry that quenches to the lowest energy classical isomer. As seen in the figures, once the vicinity of the lowest energy classical structure has been reached, transitions to configurations that quench to other isomers are quite rare at this temperature.

ters to be appreciable. We find, for example, that the quantum-mechanical ground-state energies in these clusters often exceeds the classical thresholds for cluster rearrangement. Even with this appreciable zero-point energy, however, we find that the ground-state wave functions in these systems are strongly localized about the structure of classical ground state. In related findings, finite-temperature quench studies reveal that the cluster isomerization in these systems is strongly temperature dependent, a result that suggests that the associated dynamics is activated in character.

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APPENDIX

As described in Sec. II, the DMC method exploits the isomorphism between the Schrödinger equation in imaginary time and the diffusion equation. Using this isomorphism, one "solves" the quantum-mechanical problem numerically by using random-walk methods originally designed for the simulation of ordinary diffusion processes. As discussed elsewhere,²⁵ the DMC method is exact only in the limit that the time step used in modeling the temporal evolution of the diffusion process tends to zero. In practice, acceptable values for the time step were established by performing calculations for a range of parameters and requiring that the associated systematic error in the calculation be smaller than the associated statistical error in the calculations. This range varied with the system under study, but was typically 100 a.u. (2.4×10^{-15} s) or smaller in the present neon studies. For example, step sizes of 100, 200, and 400 a.u. produced DMC estimates to the total energy of Ne₂ of $-0.5667(3)\epsilon$, $-0.5662(4)\epsilon$, and $-0.5668(4)\epsilon$, where the numbers in parentheses indicate the statistical uncertainties in the associated total energies.

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