Ab Initio Monte Carlo Investigations of Small Lithium Clusters

Sudha Srinivas\textsuperscript{1,2} and Julius Jellinek\textsuperscript{2}

\textsuperscript{1}Department of Physics, Central Michigan University, Mt. Pleasant, MI 48859, USA
\textsuperscript{2}Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

Structural and thermal properties of small lithium clusters are studied using ab initio-based Monte Carlo simulations. The ab initio scheme uses a Hartree-Fock/density functional treatment of the electronic structure combined with a jump-walking Monte Carlo sampling of nuclear configurations. Structural forms of Li\textsubscript{8} and Li\textsubscript{9}\textsuperscript{+} clusters are obtained and their thermal properties analyzed in terms of probability distributions of the cluster potential energy, average potential energy and configurational heat capacity all considered as a function of the cluster temperature. Details of the gradual evolution with temperature of the structural forms sampled are examined. Temperatures characterizing the onset of structural changes and isomer coexistence are identified for both clusters.

1. Introduction

A good theoretical account of the temperature dependent behavior of the physical properties of a cluster requires (a) an accurate depiction of the underlying interactions of its constituent entities and (b) a reliable means of obtaining the representative configurational states of the system at finite temperatures. In practice, first-principles methods or semi-empirical potentials are used for the former and simulation techniques such as Monte Carlo and molecular dynamics methods provide the statistically significant sampling required for the latter. In general, one expects a higher degree of accuracy from first principles methods such as quantum chemistry techniques and density functional theory. Most of the detailed studies on the dynamical and thermal properties of atomic clusters however utilize semiempirical potentials.

\textsuperscript{1} email: srinivas@phy.cmich.edu
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
which are computationally more efficient. These are typically pair or many-body potentials fitted to reproduce first-principles calculations for small clusters (dimer, trimer) and/or experimental properties of the bulk. Monte Carlo (MC) and molecular dynamics (MD) simulations using such potentials have provided a practical and efficient means of tackling an otherwise intractable problem and extensive information on the manner in which structural and phase transitions occur in clusters has emerged from these studies. First-principles calculations on the other hand, have typically concentrated on the static (T = 0 K) ground state properties of clusters, such as isomeric forms, binding energies, ionization potentials and other electronic and spectroscopic properties. While these studies have contributed substantially to our understanding of atomic clusters, there are obvious reasons to go beyond static properties and study structural, dynamical and thermal properties of clusters as well, at a first-principles level. The isomerization processes a cluster undergoes, the barriers between different isomers, the thermal stability of the cluster, the structural and phase transitions that occur, are all important properties of clusters. In cases where two or more isomers of a cluster lie within a very small energy range – a phenomenon that is not rare in atomic, and especially metal, clusters – it is important to examine how the cluster samples its potential energy surface at finite temperatures. Over the past decade considerable effort has gone into the development of first principles-based dynamical [1-9] and Monte Carlo [10-15] schemes many of which have found applications in the study of atomic clusters.

The large majority of ab initio MD studies have concentrated on issues related to structural forms (isomers) of clusters and changes in these forms (isomerizations). A few have also addressed issues related to the dynamics of these changes. For example, Sung, Kawai and Weare [3], Jones, Lichtenstein and Hutter [4] and Gibson and Carter [5] have all studied the pseudorotation of Li₅ clusters using Car-Parinello or generalized valence bond and complete active space self consistent field approaches. Recent ab initio molecular dynamics studies have investigated details of both structural and dynamical characteristics of lithium clusters using Hartree-Fock [6-8] calculations for neutral and cationic Liₙ clusters (6 ≤ n ≤ 11) and density functional theory [9] for Li₈.
An alternate method that facilitates the investigation of the issues (structural and phase transitions, thermal properties etc.) mentioned above is one that combines an ab initio treatment of electronic structure with a Monte Carlo rather than a dynamical sampling of nuclear configurations. Monte Carlo offers several important advantages over molecular dynamics simulations, especially in cases where structural and thermal properties are of interest. The MC sampling involves exploring the configuration space, without the computationally expensive task of calculating the energy gradients (forces) at each step. An added advantage is the fact that temperature in the MC sampling scheme is the true thermodynamical (as opposed to dynamical) temperature and the canonical Monte Carlo method directly yields the thermal properties of the system. The concept of combining a first-principles calculation of energies with a Monte Carlo scheme is not a novel one. Recently, structural properties of Li$_3$H have been examined \[10\] using an MC sampling of the nuclei with a second-order Möller-Plesset (MP2) treatment of electronic structure. Other investigations \[11-13\] have used perturbative or hybrid first-principles methods in classical Monte Carlo simulations to study the interactions of various ions with water clusters. Two recent works \[14,15\] use classical and path integral Monte Carlo sampling techniques combined with density functional theory, in one case, to study interactions of HCl with water clusters \[14\] and in the other, to investigate the quantal effects in small lithium clusters (Li$_4$ and Li$_5^-$)\[15\]. However, none of the studies mentioned above have been concerned with details of the thermodynamic properties of the system under investigation and the length of the MC sampling in these studies have been short (\(\sim 10^3\) to \(10^4\) steps).

Currently, the applicability of ab initio-based MD and MC investigations as tools to probe the finite temperature behavior of clusters is limited to small systems – the calculations involved are too expensive to achieve the level of sampling required for a detailed analysis. Small lithium clusters are ideal prototypes for studies such as these with few enough electrons that the calculations are computationally feasible, yet complex enough that interesting information emerges from ab initio investigations \[3-9,15-24\]. An important issue is the task of achieving a balance between the need to treat all the interactions in the system as accurately as possible and the requirement of a sufficiently complete sampling of nuclear
configuration space. We present a description of the structural and thermal properties of lithium clusters, at an ab initio level, in a study that we believe satisfies this criteria. The scheme uses a hybrid Hartree-Fock (HF)/density functional theory (DFT) calculation of configurational energies combined with a jump-walking [25] Monte Carlo sampling of configurational space to study the structural and thermal properties of Li₈ and Li₉⁺ clusters. The methodology used is described in the next section. The results obtained for the structural and thermal properties are analyzed in section 3 and summarized in section 4.

2. Methodology

The two major components of the scheme are the ab initio calculation of the electronic structure followed by a Monte Carlo sampling of the nuclear configuration space. The configurational energy at each step is calculated using a hybrid HF/DFT scheme, where the converged Hartree-Fock electron density ρ(r) is used in the Lee-Yang-Parr [26] (LYP) correlation functional to obtain the correlation correction to the Hartree-Fock energy. A single numerical integration is performed at each step for the calculation of the correlation energy in this formalism and represents a considerable saving in computational time. The exchange energy used is the exact Hartree-Fock exchange. The validity of using the Hartree-Fock density in a correlation functional has been addressed [27,28] and applied successfully [29] to study the binding energies of different systems. The basis set used for Li in our calculations is a (411/1) set of contracted Gaussian type orbitals (CGTO) which has been used in previous work [6-8,24]. The parallelization and optimization of the ab initio scheme – the Hartree-Fock calculations of the configurational energies and the Lee-Yang-Parr correlation correction to this energy – is described in detail in our earlier work [24] on Li₈ clusters. This parallelization is an important factor in our ability to perform the Monte Carlo simulations efficiently and obtain the level of sampling that is necessary for examining the thermal averages for the systems under investigation in the present work.

A jump-walking (j-walking) Monte Carlo scheme augments the regular Metropolis moves. The j-walking technique [25] offers a means of increasing the efficiency of sampling of the nuclear
configuration space by providing a route through which the system can avoid being trapped in one of the local minima. The problem of getting trapped in a local minimum is a particular concern at low to intermediate temperatures in the canonical Metropolis Monte Carlo [30] scheme. It is less probable at high temperatures, where the system samples many different isomeric forms, as well as at very low temperatures, where the global minimum is the most likely one. The j-walking scheme involves occasional sampling from a distribution of configurations generated at a higher temperature by a (previous) Monte Carlo sampling. The j-walker configurations at each temperature are generated in our simulations by storing every 100th configuration during a Monte Carlo sampling at that temperature. The spacing of the temperature intervals for the j-walking Monte Carlo sampling is such that approximately 50% of attempts to jump to the higher temperature j-walker configurations are accepted. The probability of acceptance is appropriately weighted so that the accepted j-walker configuration (originally generated at a higher temperature) follows the correct Boltzmann probability for the sampling temperature. At the highest temperature simulation, the Metropolis Monte Carlo procedure is the one used, while at every subsequent simulation, a j-walking Monte Carlo sampling is used, which in turn generates the j-walker configurations representative of the sampling temperature.

At each step of the Monte Carlo simulation, a randomly chosen atom is moved through random displacements in the x, y and z-directions. The maximum displacement is chosen such that the acceptance rate over the entire run at each temperature is approximately 50%. Independent random number generators with different initial seeds are used for each of the independent quantities to ensure that no correlation exists between these physical quantities. Each simulation performed at a particular temperature generates a representative Boltzmann weighted set of configurations and involves regular Metropolis moves interspersed with jump-walking attempts. Jumps are attempted at random approximately 10% of the time, to randomly chosen stored j-walker configurations. The interaction energy $V$ for each configuration is given as the difference between the total energy of that particular configuration and the sum of the energies of the constituent atoms/ion at infinite separation, all calculated
within the HF/LYP scheme. The averages of all the physical quantities are calculated over the entire length of the simulation, which is typically 300,000 to 400,000 steps in our calculations.

The physical quantities of interest in our investigations of the thermal properties of the cluster are the probability distribution function for the potential energy $V$, the average potential energy $\langle V \rangle$ and the configurational heat capacity (at constant volume) $C_v$. The latter is calculated using the expression for the heat capacity of a canonical ensemble,

$$C_v = \frac{\langle V^2 \rangle - \langle V \rangle^2}{kT^2},$$

where $V$ is the potential energy of the cluster, $k$ is the Boltzmann constant, and $\langle \cdots \rangle$ denotes the averaging over an entire MC sampling at a given temperature, $T$. The configurational heat capacity, which is a measure of the energy fluctuations in the system, is a quantity highly sensitive to small changes in the configurational energies sampled. Changes in $C_v$ herald the onset of structural or phase transitions in the system.

The different isomers of the cluster are obtained through a simulated cooling procedure within the Monte Carlo scheme, using as a starting point, configurations sampled during high temperature simulations. The quenching technique used follows a combination of two scenarios. In the first, the MC sampling is combined with a step-wise reduction of the temperature, decreasing the temperature in steps that vary from about 5% to 15% of the previous temperature at each simulation. The maximum displacement is adjusted to give an acceptance rate of approximately 50%. This is performed repeatedly until a final temperature of $10^{-3}$ K is reached. In the second scenario, only moves that lower the energy of the cluster are accepted. This process of thermal cooling is performed until the variation in the total configurational energy of the cluster remains less than $10^{-7}$ hartree ($2.7 \times 10^{-6}$ eV). All computations were performed using a parallel 12-node cluster of DEC-3000/700 workstations and a parallel 8-node cluster of DEC alpha 500/333 workstations.
3. Results and Discussion

3.1 Li₈

Four isomers are obtained for Li₈ – a lowest energy Tₐ structure, followed by two nearly degenerate Cᵥ and C₅ structures, which are 0.18 eV and 0.21 eV higher in energy than the Tₐ structure, and a highest energy (ΔE=0.58 eV) D₂d structure (Fig. 1). We also find that inclusion of correlation in this hybrid scheme marginally lowers the energy spacing between the first three isomers and significantly increases the energy spacing for the highest energy isomer (D₂d) in comparison with those obtained at the Hartree-Fock level.

The distribution of the energies sampled as a function of temperature is shown in Fig. 2, where each panel shows the normalized probability distributions for the potential energies sampled by the cluster during each j-walking Monte Carlo simulation. The smoothness of the graphs, which represent histograms obtained for a very fine mesh of energy intervals (0.00136 eV), indicate that our results are well-converged. An examination of Fig. 2 shows that at low temperatures, the probability distributions for the energies are especially narrow and have a high peak centered around lower configurational energies. The narrowness of the distribution is due to the fact that the only configurations sampled up to a temperature of about 120 K are those associated with the lowest energy isomer - the Tₐ structure, which has a binding energy of 6.38 eV. This is verified using simulated rapid cooling from many configurations generated from our sampling. The only structure that emerges in the quenches of numerous configurations associated with the 120 K sampling is the Tₐ isomer. As the cluster temperature increases, wider ranges of energies are sampled, with more of the configuration space now accessible to the system. Just above 120 K (in fact at 170 K, the next temperature sampled in the MC simulations), the second and third isomers - the C₃ᵥ and the C₅ structures make their first appearance. These two isomers have very similar packing and are very close in energy – the difference in their binding energies is less than 0.03 eV – so they easily interconvert. The fourth and highest energy isomer with the D₂d symmetry is only present among the configurations sampled at temperatures above 300 K.
Fig. 3a shows a graph of the average potential energy of the cluster as a function of the cluster temperature – the caloric curve. The averaged potential energy at each temperature of the caloric curve is obtained by averaging over the entire potential energy distribution (Fig. 2) at that temperature. Fig. 3b shows the variation of the configurational heat capacity of the cluster with temperature. Changes in the curvature of the caloric curve and the presence of a peak in the configurational heat capacity signify the occurrence of a phase transition. Clusters are known to exhibit a broad peak in their heat capacity, indicating a gradual, stage-wise melting-like transition [31-36], rather than the sharp transitions found in bulk. The presence of an inflection in the caloric curve over a wide temperature region between 180 K-400 K signifies the occurrence of this type of transition. The phenomenon is even more dramatically illustrated by the behavior of the configurational heat capacity, whose graph shows a very broad peak starting at a temperature of around 120 K, with the maximum value of $C_v$ occurring in the region around 420 K-430 K.

### 3.2 Li$_9^+$

The three isomers obtained for Li$_9^+$ are shown in Fig. 4. The lowest energy isomer of Li$_9^+$ is a distorted antiprism-type structure with a central atom and has a $D_{4d}$ symmetry. The next higher energy isomer is a $C_{2v}$ structure ($\Delta E=0.088$ eV) and the third isomer has a $C_{3v}$ geometry and is 0.242 eV higher in energy than the lowest energy isomer. Our calculations show that in the case of Li$_9^+$, the energy spacing between the three isomers increases marginally with the inclusion of correlation, as compared with that obtained at a Hartree-Fock level.

The normalized distributions of the potential energies sampled by the cluster in our Monte Carlo simulations for different temperatures are illustrated in Fig. 5. The histograms shown in the above use an energy interval of 0.00136 eV as the sorting box size. As in Li$_8$, the potential energy distributions are characterized by narrow, high peaks at low temperatures, where the sampling takes place in the region of the lowest energy isomer(s), and broad, low peaks at higher temperatures, as more of the configuration
space becomes accessible to the cluster. Our simulations show that below 75 K, the only isomer that is sampled is the lowest energy $D_{4d}$ isomer, which has a binding energy of 8.90 eV in its equilibrium geometry. At around 75 K, the second lowest energy structure (the $C_{2v}$ isomer — which has a binding energy of 8.81 eV) should, in principle, be accessible from energy considerations. However, we see configurations associated with the second isomer being included in the sampling only at temperatures of 125 K and above. By 175 K, all three isomers of Li$_9^+$ are present in the sampling.

The caloric curve obtained for Li$_9^+$ is shown in Fig. 6a. The behavior of the configurational heat capacity as a function of the temperature is shown in Fig. 6b. The graph shows an increase in the heat capacity beginning at a temperature of about 125 K. The peak in the configurational heat capacity is a rather "soft" one and occurs at a temperature of about 300 K. The simulations indicate a significant amount of structure present in the configurational heat capacity in the region between 300 K and 420 K, which could be a signal of additional changes taking place or could be the consequence of inadequate sampling in this region. We have been unable to resolve this structure in the simulations performed with increased lengths (5 ~ 6 x $10^5$ steps) of sampling.

The characteristics of the solid-to-liquid-like transition experienced by a cluster — the temperatures at which individual isomers make their appearance and the temperature range in which the structural and phase transitions occur — are intimately linked to details of the energy landscape, such as the energy ordering of the isomers and the barriers between different isomers. Our results for Li$_8$ and Li$_9^+$ clusters illustrate this dependence. The temperatures at which the higher energy isomers become accessible in the sampling are 125 K for the sampling of the second and third isomers (which are almost degenerate) and 300 K for sampling of all the four isomers of Li$_8$. In the case of Li$_9^+$, where the three isomers are more closely spaced, only the lowest energy isomer is sampled up to a temperature of 100 K. The second isomer gets added to the sampling at temperatures above 100 K, and the catchment areas of all three isomers of Li$_9^+$ are accessible to the cluster by 175 K. The lower characteristic temperatures obtained for Li$_9^+$ as compared with those for Li$_8$ are consistent with our observation of smaller energy spacing between
the isomers of $\text{Li}_5^+$ present in the sampling as compared with the energy spacing between isomers of $\text{Li}_8$. The melting-like transition, where the cluster goes from a solid-like stage associated with a single isomer to a liquid-like stage where all structures are sampled, thus occurs over a wide temperature range for both clusters. It should be noted that the melting temperature for bulk lithium is 453K.

4. Summary

We have presented a brief outline of an efficient ab initio Monte Carlo scheme utilized to study the structural and thermal properties of $\text{Li}_8$ and $\text{Li}_9^+$ clusters. The scheme combines a hybrid Hartree-Fock/density functional treatment of electronic structure with a jump-walking version of the Monte Carlo sampling. Parallelization of the ab initio part of the calculations and the inclusion of j-walking contribute to rendering this scheme very efficient – the former from the viewpoint of the time spent in the calculation of configurational energies and the latter for an adequate sampling of the configuration space. It is worthwhile to comment on some of the differences between this work and previous ones, namely, the HF and DFT-based molecular dynamics studies on lithium clusters [6-9]. While the MD investigations have carried out studies that involve very extensive sampling – certainly among the most exhaustive investigations performed to date with ab initio dynamics – there are some unresolved features. For example, it is difficult when comparing these studies, to accurately pinpoint whether the differences in the temperatures characterizing the onset of isomerizations in the cluster within the two approaches, arise from the absence (HF) or presence (DFT) of correlation or from the fact that the "dynamical temperature" of the cluster may not accurately represent the "thermodynamical temperature" of the cluster at those sampling lengths. In the alternate ab initio based Monte Carlo sampling scheme adopted in our work, the cluster temperature is a well-defined thermodynamical parameter regardless of the length of the simulation, and the temperatures characterizing the onset of isomerizations quoted here are meaningful quantities.
At present, when there is little experimental data on the isomer-specific thermal properties of atomic clusters, ab initio theoretical studies such as these provide a means to understand the nature and mechanism of structural and phase transitions in clusters. The study enables us to characterize, at a first-principles level, the temperatures at which a specific cluster undergoes structural transitions, and to pinpoint regions of isomer co-existence. From a practical viewpoint, the characterization of the temperatures at which structural changes occur is expected to aid in the structural identifications of the isomers present in cluster beam experiments carried out at finite temperatures.

Acknowledgments

The work presented was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, US-DOE under contract number W-31-109-ENG-38.
References


D. Hohl, R. O. Jones, R. Car and M. Parrinello, J. Chem. Phys. 89, 6823 (1988);
R. Kawai and J. H. Weare, Phys. Rev. Lett. 65, 80 (1990);
N. Binggelli, J. L. Martins and J. R. Chelikowsky, Phys. Rev. Lett. 68, 2956 (1992);

3. M. -W. Sung, R. Kawai and J. H. Weare, Phys. Rev. Lett. 73, 3552 (1994);


21, 1087 (1953); A detailed description of the Metropolis Monte Carlo scheme is provided in J. P.

31. R. S. Berry, T. L. Beck, H. L. Davis and J. Jellinek, in The Evolution of Size Effects in Chemical
Dynamics, Advances in Chemical Physics, Eds I. Prigogine and S. A. Rice, Wiley-Interscience,
New York 1988, 70(2), (p. 75).

32. J. Jellinek, in Metal-Ligand Interactions, Eds N. Russo and D. R. Salahub, Kluwer Academic
Publishers, Dordrecht 1996 (p. 325) and references therein.


Figure Captions

Figure 1. Isomers of Li$_8$ obtained within the HF-LYP MC scheme. The numbers are the energy gaps (in eV) between the lowest energy $T_d$ structure and the higher energy isomers.

Figure 2. Histograms of the normalized probability distribution of the potential energy of Li$_8$ at different temperatures. The probabilities are calculated with an energy box size of 0.00136 eV. The equilibrium energies of the isomers are indicated by arrows.

Figure 3. (a) Averaged potential energy of Li$_8$ as a function of temperature. (b) Configurational heat capacity of Li$_8$ as a function of temperature.

Figure 4. Isomers of Li$_9^+$ obtained within the HF-LYP MC scheme. The numbers are the energy gaps (in eV) between the lowest energy $D_{4d}$ structure and the higher energy isomers.

Figure 5. Histograms of the normalized probability distribution of the potential energy of Li$_8$ at different temperatures. The probabilities are calculated with an energy box size of 0.00136 eV. The equilibrium energies of the isomers are indicated by arrows.

Figure 6. (a) Averaged potential energy of Li$_9^+$ as a function of temperature. (b) Configurational heat capacity of Li$_9^+$ as a function of temperature.
$T_d$
$\Delta E = 0.0 \text{ eV}$

$C_{3v}$
$\Delta E = 0.182 \text{ eV}$

$C_s$
$\Delta E = 0.206 \text{ eV}$

$D_{2d}$
$\Delta E = 0.584 \text{ eV}$
\begin{figure}[h]
\centering
\subfigure[]{
\includegraphics{figure_a.png}
\caption{\textbf{Figure 3a}: 
\emph{\textbf{Figure 3a}} depicts the relationship between \textbf{\textless} \textit{V} \textgreater \textbf{(eV)} and temperature.}
}
\subfigure[]{
\includegraphics{figure_b.png}
\caption{\textbf{Figure 3b}: 
\emph{\textbf{Figure 3b}} illustrates the variation of \textbf{C\textsubscript{v} (eV/K)} with temperature.}
\end{figure}
\[ \Delta E = 0.0 \text{ eV} \]
\[ \Delta E = 0.088 \text{ eV} \]
\[ \Delta E = 0.242 \text{ eV} \]