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Delocalization and tunneling in the ionic structure of lithium microclusters

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Quantum effects in the ionic structure of lithium microclusters Li_n have been estimated by applying a simple Hamiltonian to model selected cluster sizes ($n = 20$, 40, and 92). Equilibrium structures and thermodynamic properties are computed with use of the path-integral Monte Carlo method. The results show that quantum effects play an important role up to relatively high temperatures. Zero-point motion and tunneling enhance the tendency to disorder already implicit in the delocalized bonding of alkali-metal clusters. The model predicts that, up to the sizes analyzed here, the clusters are fluidlike at all temperatures.

Favorable physical properties and the simplicity of their electronic structure have made the alkali metals the key elements for the experimental and theoretical investigation of atomic microclusters.[1] Following the groundbreaking work by Knight *et al.*,[2] several studies have established the validity of the jellium model to describe alkali-metal clusters. The shape, stability, polarizability, ionization potential, etc., of these clusters depend in a simple and characteristic way on the number n of valence electrons. Special numbers, corresponding to the filling of the angular momentum levels in a smooth, spherical potential, identify spherical and particularly stable clusters.

Sodium is the obvious prototype for this kind of description, which, however, remains valid with only minor deviations for lighter (lithium) and heavier alkali metals. The anomalies observed for Li clusters[3] are mainly explained in terms of the properties of its ionic core. The tiny Li^+ ion contains only s electrons, and does not provide any orthogonalization repulsion for the $l > 0$ states. This implies an enhanced hybridization of s and p states in the formation of cluster orbitals, and a deviation from the jellium model.[4,5]

The other important peculiarity of Li is its very light mass, whose effect on optical properties is well recognized for the solid.[6] Much less attention has been devoted to this peculiarity in the case of clusters. To our knowledge, the theoretical investigation of ionic quantum effects has been limited to very small sizes. In a very early paper, Gerber and Schumacher[7] pointed out the importance of vibronic coupling in the ground state of Li_3. Their computation was refined and extended to other alkali-metal trimers by Martins, Car, and Buttet[8] and confirmed experimentally by Wolf, Delacrétaz, and Wöste.[9]

In the present paper we extend the analysis of ionic quantum effects to larger clusters, and we systematically study the role of temperature. A simple model allows us to perform extensive path-integral Monte Carlo[10] simulations. Our results show that, up to relatively high temperatures, zero-point motion and tunneling play a crucial role in the determination of the structural and thermodynamic properties of these systems.

In our computation we resort to a finite version of the one-component plasma (OCP) extensively studied in classical statistical mechanics.[11,12] In this model, in many respects complementary to the jellium model, the electrons are replaced by a uniform background of negative charge at the density ρ corresponding to the bulk valence electron gas parameter r_s $(1/\rho = \frac{4}{3}\pi r_s^3)$. The Li ions are represented by positive point charges. The OCP is known to provide a good first approximation to the structural and dynamical properties of alkali metal.[13] In particular, the OCP offers good thermodynamic functions for the ionic contribution to the metal free energy. It has also been extensively used to model alkali-metal surfaces[14] and, more recently, it has been introduced in the field of clusters by Manninen.[15]

The usefulness of the OCP as a first-order approximation for the ionic structure of alkali metals rests on (i) the free-electron approximation for the electronic structure; (ii) a weak dependence of the electronic properties on temperature; (iii) the relative insensitivity of the electronic configuration on the ionic positions; (iv) the importance, if not the dominance, of the Madelung energy (i.e., the only contribution to the potential energy retained in the present model) in the determination of the ionic structure. Several arguments, widely discussed in the literature,[11–13] justify the validity of (i)–(iv) for extended systems. For alkali-metal clusters, the fair agreement of experiments with the predictions of the jellium model supports approximations (i) and (ii). Moreover, *ab initio* computations show that (iii) and (iv) are satisfied to a reasonable extent.[16,15,17] Other points of contact with *ab initio* results will come out of our results, and are discussed below. Of course, the OCP offers only a primitive description of alkali-metal clusters, and in particular of Li aggregates, for which the deviation from the free-electron behavior is not negligible. We believe, however, that this does not prevent the applicability of the model to highlight the importance of quantum-mechanical features in the structure of these systems.

The Hamiltonian we use is

$$H = \sum_{i=1}^{n} \frac{P_i^2}{2M} + \sum_{i=1}^{n} \varphi(|\mathbf{r}_i|) + \frac{1}{2}\sum_{i \neq j} \frac{1}{r_{ij}} ,$$

where M is the mass of the Li^+, and the first term is the ionic kinetic energy. $\varphi(r)$ is the electrostatic potential of the spherical background neutralizing the system. The last term is the Coulomb interaction of the n Li^+ ions. Hartree's atomic units are used throughout the paper.

The assumption of spherical background will limit our analysis to the numbers n corresponding to electronically spherical clusters. The computations presented below are for $n=20$, 40, and 92. Since de Broglie's thermal wavelength is comparable to the interparticle distance only at very low T, we neglect exchange and we treat the ions as distinguishable.

The equilibrium properties of the system at a temperature T are obtained from the canonical partition function:

$$Q_n(T) = \mathrm{Tr}\exp(-\beta H) ,$$

where $\beta = 1/(k_B T)$ and k_B is the Boltzmann constant.

In the classical limit (large M or T) the equilibrium properties are computed by standard Monte Carlo averages. In the quantum-mechanical case (finite M and low T) the equilibrium properties are computed via the path-integral Monte Carlo (PIMC) method. This method is described in detail elsewhere.[10,18] We only remind the reader that the quantum problem is mapped onto a classical Hamiltonian in which each of the ions is represented by P interacting particles (the "polymer" isomorphism). The appropriate value of P depends on the mass M, the temperature, and the steepness of the potential. In our computation we took $P=2880/T$. Since this is not an extreme value (the $1/r$ potential is indeed very soft), sampling the configuration space was not a problem, and we restricted ourselves to the so-called "primitive algorithm."[19]

Before presenting the PIMC simulation, we first discuss the results of the classical limit ($M \rightarrow \infty$). For the three n's considered here, simulated annealing from high T (~ 600 K) provides compact ground-state (GS) structures, with a nearest-neighbor (NN) distance of 5.2, 5.4, and 5.65 a.u. for $n=20$, 40, and 92, respectively, to be compared with the experimental NN distance spanning the interval 5.05–5.7 a.u. in going from Li_2 to the solid. The first and second coordination shells in the radial distribution function $g(r)$ are slightly compenetrating, thus suggesting atomic configurations not completely ordered even at $T=0$. For Li_{20} the qualitative features of our GS structure (as characterized by interatomic distances, radial, and angular distribution functions) are not very different from those provided by an *ab initio* computation.[5]

Monte Carlo (MC) simulations confirm the importance of structural disorder down to very low T. Repeated quenches during the MC runs reveal a number of isomers almost degenerate in energy with the GS. Barriers among the local minima are low, and even at the lowest simulated temperature ($T=30$ K) ions are able to migrate from one configuration to another one. As a consequence, the one-body density and the radial distribution function present an important broadening already at low T. The mean-square displacement (computed over a fixed number of MC steps) increases smoothly with T. For the three sizes examined here, the specific heat $C(T)$ shows no sign of anomalies reminiscent of the solid-liquid or other structural phase transitions (see Fig. 1).

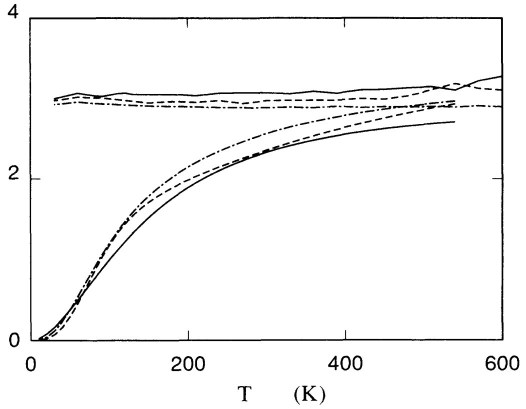

FIG. 1. Specific heat per particle C/k_B as a function of temperature for Li_{20} (full line), Li_{40} (dashed line), and Li_{92} (dash-dotted line) computed by classical MC and PIMC. The low-T behavior distinguishes the classical ($C \rightarrow 3k_B$) from the quantum results ($C \rightarrow 0$).

We defer a critical discussion of this behavior to the conclusions, and we turn to the results of the PIMC simulation, showing that delocalization and tunneling strongly enhance this tendency of Li clusters to a fluidlike phase at low T.

In Fig. 2 we compare the one-body density profile $\rho(r)$ for Li_{40} at $T=30$ K computed by classical MC and PIMC. The classical result, displaying two sharp ionic shells, is significantly broadened by quantum delocalization. The two shells, however, remain well defined and separated even in the quantum model.

More important are the effects on the radial distribution function $g(r)$, reported in Fig. 3 for $T=30$ K.[20] Quantum delocalization is again apparent in the broadening of the first peak, the blurring of the fine structures, and in the reduction of the distance of closest approach between the ions. Periodic quenches of the PIMC

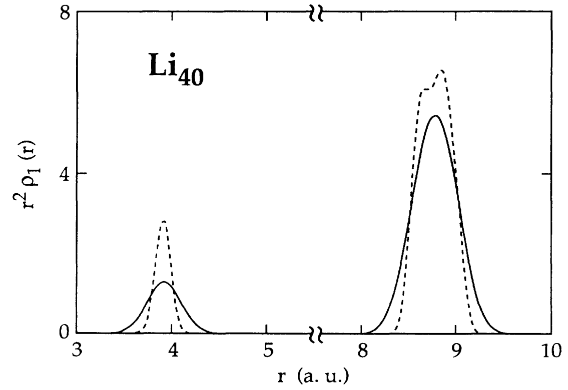

FIG. 2. Spherical average of the one-body density ρ_1 (times r^2) as a function of distance r from the center of mass of Li_{40} at $T=30$ K. Full line: PIMC computation. Dashed line: classical computation.

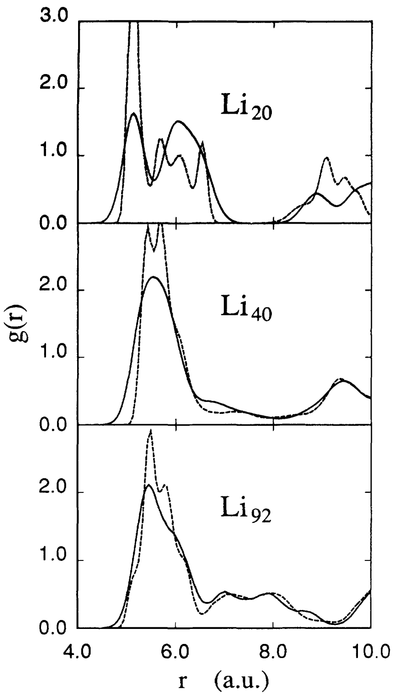

FIG. 3. Radial distribution function $g(r)$ for Li_{20}, Li_{40}, and Li_{92} at $T=30$ K. Full line: PIMC computations. Dashed line: classical computations.

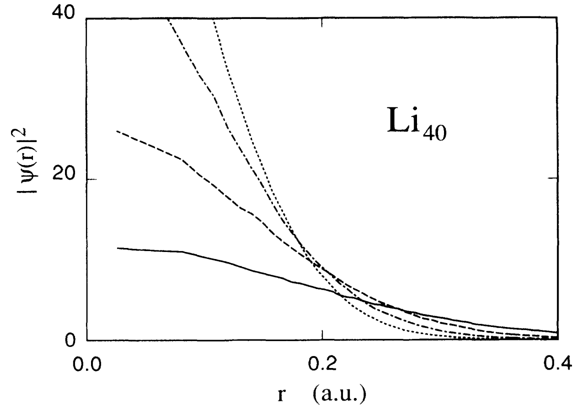

FIG. 4. Spherical average of the modulus square of the wave function of a single ion as a function of distance from the instantaneous center of mass of the ion itself. Full line: 30 K. Dashed line: 90 K. Dashed-dotted line: 150 K. Dotted line: 210 K.

configurations shows path-integral "polymers" stretching between different local minima, thus explicitly identifying tunneling ions.

The analysis of these snapshots shows that the isomers involved in the tunneling process differ mainly for the position of the ions in the outermost incomplete ionic shell. This explains the different importance of quantum effects on $\rho_1(r)$ and $g(r)$, and suggests that sizes corresponding to closed *ionic* shells could behave differently from the clusters examined here. Given the crucial role of the intrinsic defects in the outermost shell, it could be more appropriate to talk of surface fluid behavior. However, we will not make such a distinction, since in these small systems the atoms in the outermost layer are the great majority and dominate the properties of the cluster.

The specific heat $C(T)$ of the quantum model is computed by derivation of a Padé fit to the total energy as a function of T. $C(T)$ vanishes for $T \to 0$. In the region of intermediate T ($30 < T < 250$ K) it is systematically higher than the specific heat of the quantum oscillators at the frequencies of the eigenmodes of the GS structures, thus confirming the importance of anharmonic effects.

Paralleling the slow rise of $C(T)$ to its classical value, we observe a much lower sensitivity of $\rho_1(r)$ and $g(r)$ on T than in the classical model. With increasing T the growing amplitude of the classical displacement is partially compensated by the localization of the ionic wave functions due to disorder. This latter effect is illustrated in Fig. 4, reporting the density distribution $|\psi(\mathbf{r})|^2$ for a single ion in the interval $30 < T < 270$ K. On average, $|\psi(\mathbf{r})|^2$ has a nearly spherical symmetry, with a radial shape well approximated by a Gaussian function. The width of the wave function decreases steadily with T, with a progression modulated by the details of the vibrational density of states.

In conclusion, we have shown that the light ionic mass and the existence of many low-energy isomers make quantum effects an essential feature in the behavior of Li clusters up to temperatures of the order of nearly room temperature.

PIMC simulations show that the structural and thermal properties of these systems evolve smoothly with T, without any anomaly reminiscent of phase transitions. This "fluidlike" behavior at all temperatures is partly due to the flatness and degeneracies of the cluster potential energy, and therefore could also be an artifact of our simple model. We believe instead that it reflects a true feature of Li clusters. First of all, the existence of a multitude of isomers and the flatness of the potential energy surface for alkali-metal clusters is well documented by *ab initio* computations.[16,5,4] Moreover, the magnitude of the quantum effects estimated by our computation is such that they could overcome barriers significantly larger than those present in our model.

We expect that similar effects will play a role also for clusters of other alkali metals, and in particular for sodium clusters. Of course, the strength of these effects and the range of T for which they are important will decrease with increasing mass and decreasing bulk Debye temperature going down the alkali-metal column. In this context, we mention that the estimated cluster temperature of recent beam experiments is as low as 30 K.[21]

Work is planned to estimate the importance of exchange at $T=0$ K and to evaluate the differences in the behavior of the two isotopes(^{6}Li and ^{7}Li) of lithium.

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