Structural Transformations and Melting in Neon Clusters: Quantum versus Classical Mechanics

Pavel A. Frantsuzov, Dario Meluzzi, and Vladimir A. Mandelshtam
Chemistry Department, University of California at Irvine, Irvine, California 92697, USA
(Received 17 November 2005; published 20 March 2006)

The extraordinary complexity of Lennard-Jones (LJ) clusters, which exhibit numerous structures and ''phases'' when their size or temperature is varied, presents a great challenge for accurate numerical simulations, even without accounting for quantum effects. To study the latter, we utilize the variational Gaussian wave packet method in conjunction with the exchange Monte Carlo sampling technique. We show that the quantum nature of neon clusters has a substantial effect on their size-temperature ''phase diagrams,'' particularly the critical parameters of certain structural transformations. We also give a numerical confirmation that none of the nonicosahedral structures observed for some classical LJ clusters are favorable in the quantum case.

DOI: 10.1103/PhysRevLett.96.113401 PACS numbers: 36.40.−c, 64.60.−i, 64.70.−p

Atomic clusters exhibit very rich structural, thermodynamic, and dynamical properties that may vary with size in a nonmonotonic fashion. In particular, rare gas atomic clusters, often modeled using the Lennard-Jones (LJ) pair potential, have been very popular in the last several decades. Typically, multifunnel and rough potential energy landscapes in LJ clusters make their numerical simulations extremely challenging, even when the quantum effects are neglected. In the past, a number of publications addressed the role of the latter using the path integral Monte Carlo (PIMC) method. A particularly interesting case corresponds to neon clusters (see, e.g., Refs. [1,2]). However, for a system as small as Ne_{13} a well-converged heat capacity $C_V(T)$ was reported only recently [2]. Such a calculation is apparently a rather difficult task. In Ref. [3] the most recent version of a PIMC heat capacity estimator [4] was applied to compute $C_V(T)$ for Ne_{38}, but the convergence at low temperatures was not quite satisfactory. In the same paper, the variational Gaussian wave packet (VGW) method was also applied to Ne_{38}. Although manifestly approximate, the latter method had so far demonstrated both numerical efficiency and surprisingly high accuracy when compared to the exact results for low dimensional systems [5] or to accurate PIMC calculations [6]. Unfortunately, its application to a system as complex as Ne_{38} also seemed quite expensive. This high cost, however, was expected as accurate heat capacity calculations for the classical LJ_{38} cluster required a numerical effort several orders of magnitude greater than that required for LJ_{13} [7]. It is the relatively good convergence achieved in Ref. [3] for Ne_{38} using both VGW and PIMC methods that may seem rather surprising. Unlike its classical counterpart, due to strong quantum effects, this system has a simple single-funnel configuration space at low temperatures and does not undergo structural transformations. Otherwise, much longer Monte Carlo runs would be needed. For example, the VGW method in its original formulation [3,5] is likely to fail for the case of Ne_{39} using any reasonable computational resources.

In this Letter, in order to improve the convergence properties of the VGW method we implement a much more efficient sampling scheme based on the exchange Monte Carlo (EMC) (or parallel tempering) procedure [8,9], rather than on a single Metropolis random walk done at sufficiently high temperature [3,5]. The method is applied to compute the heat capacities for $Ne_{35–39}$. The present result for Ne_{38} has statistical errors at least an order of magnitude smaller than those in Ref. [3], but is achieved with a comparable numerical effort. We also perform the VGW analysis of the ground states of Ne_n for sizes up to $n = 120$.

First we briefly review the properties of classical LJ_n clusters. Then we contrast those with the properties of quantum Ne_n clusters.

Figure 1 shows the orientational bond order parameter Q_6 [10] obtained from the global minima of LJ_n [11] as a function of n. (Here, the choice for the order parameter Q_6 is motivated by its high sensitivity to cluster symmetry.) The two dominant structural types that are realized for all but several special cases ($n = 38, 75–77, 98, 102–104$) are based on either the Mackay icosahedral or anti-Mackay (or polyicosahedral) motifs, which correspond, respectively, to an incomplete Mackay or anti-Mackay overlayer surrounding a Mackay icosahedral core [12–15]. As seen in Fig. 1, at zero temperature the Mackay to anti-Mackay ($M \rightarrow aM$) transitions occur at sizes $31 \rightarrow 30$ and $82 \rightarrow 81$.

Depending on the structure of the global minimum, a LJ cluster may undergo one or more temperature-induced structural transformations [7,16–19] according to the following general rules. Clusters with a Mackay overlayer in the global energy minimum will, at some finite temperature, undergo a surface (melting?) transition to an anti-Mackay overlayer, because the latter is entropically more favorable than the former [17,19]. A complete melting of the cluster, which we loosely define as the ''core melting,'' occurs at higher temperatures [19] but is not always easy to characterize, especially for small two-layer clusters for which the 13-atom core may be impossible to identify

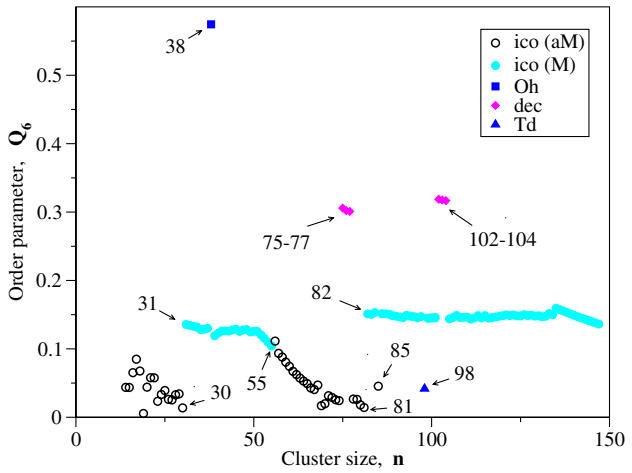

FIG. 1 (color online). Orientational bond order parameter Q_6 as a function of cluster size for global minima of classical LJ_n clusters. The following symmetry types are identified: Mackay icosahedral [ico(M)], anti-Mackay icosahedral [ico(aM)], Truncated octahedral (Oh), decahedral (dec) and Tetrahedral (Td).

uniquely. The left panel of Fig. 2 compares heat capacities of LJ_{30} and LJ_{31}. The $M \rightarrow aM$ transition in LJ_{31} gives rise to a small peak in the $C_V(T)$ curve at $T \sim 1.0$ K. (Here and throughout we assume LJ parameters for the Ne-Ne pair potential.) The core melting transition results in a broad maximum at $T \sim 11.8$ K. The $M \rightarrow aM$ transitions in bigger clusters, as in $LJ_{38,39}$ (right panel of Fig. 2), give rise to

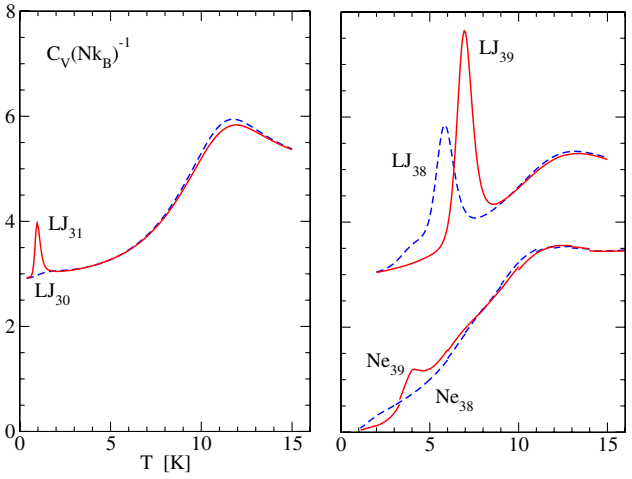

FIG. 2 (color online). Heat capacities for the classical (LJ) and quantum (Ne) clusters. The broad maxima of $C_V(T)$ at $T > 10$ K are presumably due to the cluster core melting. A shoulder in the $C_V(T)$ curve at $T \sim 4$ K for LJ_{38} is a result of the structural transformation from the global octahedral minimum toward the Mackay icosahedral local minima. $LJ_{31,39}$ and Ne_{39} at zero temperature have the Mackay overlayer (and so does LJ_{38} at $T >$ 4 K) and as such undergo the temperature-induced $M \rightarrow aM$ transitions at temperatures where the sharper peaks are situated. The thermodynamic properties of LJ_{30} and Ne_{38} are similar in that they both have anti-Mackay overlayers at $T = 0$ and do not undergo any low-temperature transitions below core melting.

peaks that are stronger and shifted to higher temperatures. Clusters with nonicosahedral global minima undergo global structural transformations at some low temperature toward icosahedral local minima, because the latter are entropically more favorable than the former [7,15,20]. Such a transition in LJ_{38} gives a little bump in $C_V(T)$ at $T \sim 4$ K and is hard to identify. However, this and the other structural transitions mentioned above are clearly characterized by the distributions $\rho(Q_6, T)$ of the orientational bond order parameter Q_6 as a function of temperature (see Fig. 3), which has distinct values for different symmetries (cf. Figure 1). These plots reconfirm that the structural transitions in finite systems are better described by coexistence regions [21], where, e.g., the distribution $\rho(Q_6, T)$ for a specific temperature range may have a bimodal character.

While much is now understood about classical LJ clusters, less can be said about the effect that the quantum nature of, say, rare gas clusters can have on their thermodynamic properties. For argon and heavier rare gas clusters, quantum effects can often be treated as small perturbations [22]. However, neon clusters are expected to exhibit strong quantum effects not only in the low-temperature regime, but also in the liquid phase [1].

By using a procedure based on VGW and similar to that of Ref. [3], we were able to estimate the ground state energies and structures of Ne_n clusters for $n \leq 105$ and $n = 110, 115, 120$. For the case of Ne_{38} the method proved to be reliable when verified by extensive PIMC calculations. Here, for each n several long random walks with classical canonical distributions are generated at a series of temperatures between 5 and 9 K using a standard EMC procedure similar to that utilized in Ref. [19]. Once in every 1000 MC steps per temperature, the cluster configuration is selected as the initial condition for propagating the VGW in imaginary time to a high value (low temperature) in order to obtain a stationary Gaussian state. We also construct the stationary states from all the configurations given in Ref. [11]. The state with the lowest energy is then accepted as a putative ground state. Since this particular calculation uses a more accurate version of the VGW method, i.e., fully correlated Gaussians, that scales numerically as n^3, it becomes prohibitively expensive for large clusters. Figure 4 displays the orientational bond order parameter Q_6 computed for the ground states as a function of n. This diagram confirms the conclusion of Ref. [22], based on the harmonic approximation (HA), that none of the nonicosahedral configurations (cf. Figure 1) survives for the quantum case of Ne_n. However, we note that in the Ne_n case, the HA gives grossly incorrect energy estimates due to the excessive value of the quantum delocalization parameter $\Lambda = \hbar/\sigma\sqrt{m\epsilon} = 0.095$, which can even lead to delocalization of the ground state over several local potential energy minima [3]. In particular, most of the ground state structures reported in Ref. [11] that are different from the classical global minima do not actually give stationary Gaussians with the lowest energy.

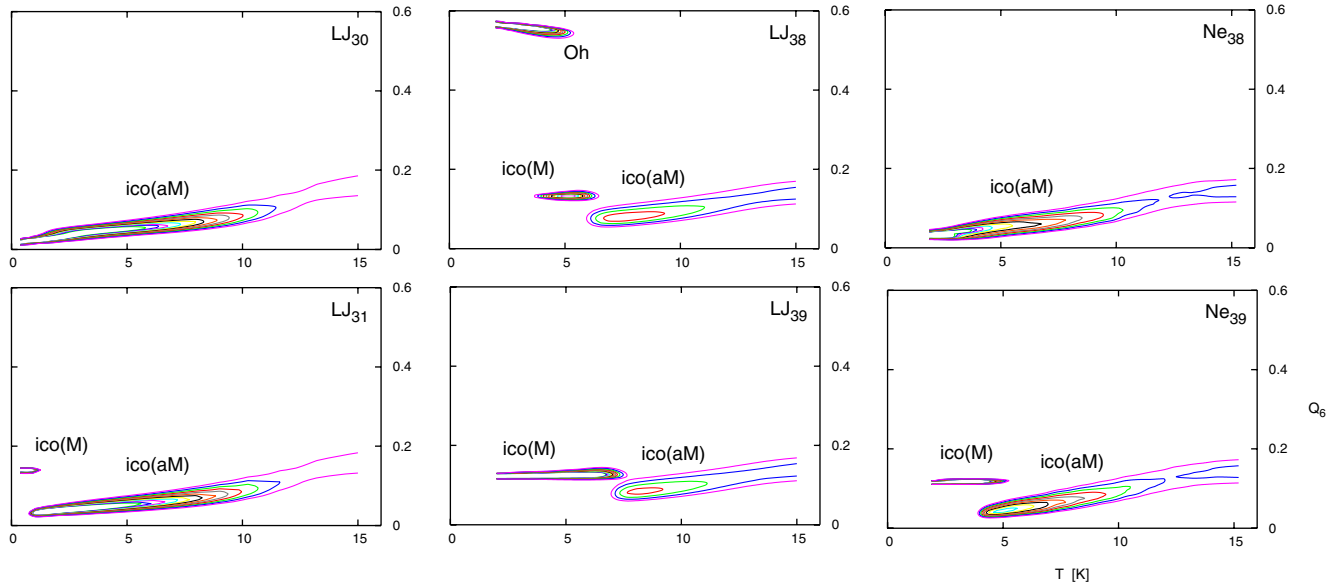

FIG. 3 (color online). Contourplots of the distributions $\rho(Q_6, T)$ of the orientational bond order parameter Q_6 for the classical (LJ) and quantum (Ne) Lennard-Jones clusters.

The quantum effects make the anti-Mackay symmetry more favorable than the Mackay symmetry, shifting the corresponding transition to higher cluster sizes. In particular, it is only starting at $n = 39$ that the ground states of all the double-layer Ne_n clusters have the Mackay symmetry and are localized over the global minimum of the potential energy. Figure 5 displays two- and three-layer neon clusters that are representative of the two symmetry types. The anti-Mackay overlayers are less compact and seem to have more liquidlike character. By analogy to the classical case [19], we expect to observe the temperature-induced $M \rightarrow aM$ transition in clusters with Mackay overlayer, while for anti-Mackay clusters the core melting at $T \sim 10$ K should be the only structural transformation.

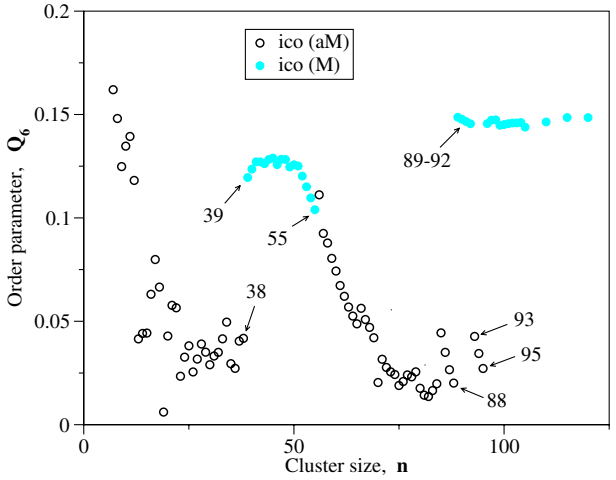

FIG. 4 (color online). Orientational bond order parameter Q_6 for the putative ground states of Ne_n clusters.

In order to support our conjecture, we performed the heat capacity calculations for Ne_{35-39} in the temperature range $1\ \text{K} < T < 16\ \text{K}$. A confining radius of $R_c = 3\sigma$ was used. While for $n \leq 38$ the convergence was relatively easy to achieve due to the lack of structural transformations at low temperatures, the results for Ne_{39} were particularly slow to converge. For this case, 14 replica temperatures T_k distributed in the temperature range of interest gave rise to 14 random walks, which were executed in a parallel fashion on a 14-processor computer cluster. During the equilibration run the temperature grid was adjusted to make the exchange rate between replicas at adjacent temperatures equal to approximately 50%. The temperature-dependent observables for each interval between the two adjacent replicas $T_k < T < T_{k+1}$ were evaluated by the method of Ref. [3] utilizing the contribution from the $(k + 1)$th replica. The convergence was monitored by comparing averages over independent successive runs. The total number of MC steps needed to obtain reasonably well-converged results for Ne_{39} was $N_{\text{MC}} \sim 4 \times 10^6$, where one MC step corresponds to one accepted Gaussian wave packet in the

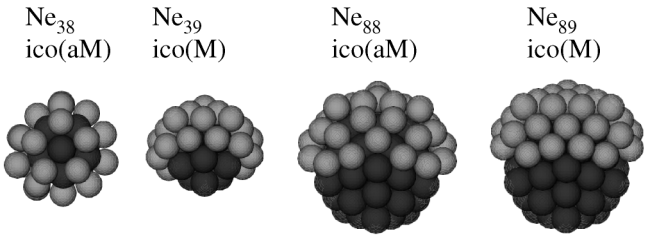

FIG. 5. Some Ne_n ground state configurations estimated by the VGW method and representative of the two possible overlayer symmetry types. (The core atoms are shown in dark color.)

Metropolis random walk for the lowest temperature replica. (In the present implementation of the parallel algorithm, different numbers of MC steps are completed per unit time at different replica temperatures, the lowest temperature replica being the slowest as it requires the longest integration in imaginary time.) Obtaining even better statistical errors for Ne_{38} required only $N_{MC} \sim 1 \times 10^6$. (A more detailed description of the computational procedure and the associated convergence issues will be reported elsewhere.)

Heat capacities of the representative quantum $Ne_{38,39}$ clusters are shown in Fig. 2 together with the corresponding classical results. [We omit the $C_V(T)$ curves for Ne_{35-37} because they appear to be very similar to that for Ne_{38}.] The small peak at $T \sim 4$ K in the $C_V(T)$ curve for Ne_{39} indicates the existence of a structural transformation at $T \sim 4$ K. Further evidence of this transformation can be obtained by comparing the order parameter distributions $\rho(Q_6, T)$ for classical LJ_n clusters (Fig. 3, left panels) with those for quantum $Ne_{38,39}$ clusters (right panels). Especially striking are the similarities between the distribution patterns of LJ_{30}-Ne_{38} and LJ_{31}-Ne_{39}, which are naturally interpreted in terms of the temperature- or size-induced $M \rightarrow aM$ structural rearrangements.

In conclusion, we have investigated thermodynamic and structural properties of quantum neon clusters using an improved version of the recently developed VGW method. Analysis of the estimated ground state structures of Ne_n clusters in the size range $n < 120$ allowed us to provide a numerical justification of the previously conjectured fact [22] that nonicosahedral structures are thermodynamically unstable. We also identified the critical sizes for the $M \rightarrow aM$ transition for Ne_n clusters.

Furthermore, the new sampling procedure based on the exchange Monte Carlo algorithm allowed us to obtain reasonably well-converged results for Ne_{39}, which displays qualitatively different and more complex behavior than Ne_{38}. Particularly, we have shown that, besides the core melting transition, Ne_{39} undergoes a temperature-induced $M \rightarrow aM$ surface structural transformation.

Although manifestly approximate, our results are practically accurate and constitute an important step forward in both constructing and understanding the ''phase'' diagram of atomic clusters. Unfortunately, an experimental confirmation of our findings appears currently impossible due to the technical challenges associated with measurements on neutral rare gas clusters. We note, though, that indications of surface melting effects have been observed in recent experiments on ionized aluminum clusters [23].

Finally, our method is not intended to replace the well established PIMC approach, which is truly a first-principles approach. Rather, we aim to provide a complementary tool for quantum statistical mechanics calculations of many-body systems.

We are grateful to Florent Calvo for very useful discussions, specifically for the suggestion to consider the distributions of the order parameter. Support from the NSF, Grants No. CHE-0414110 and No. DMS-0300974, and UCI Summer Undergraduate Research Program are acknowledged. V. A. M. thanks the Alfred P. Sloan Foundation for financial support.

[1] D. D. Frantz, D. L. Freeman, and J. D. Doll, J. Chem. Phys. **97**, 5713 (1992); T. L. Beck, J. D. Doll, and D. L. Freeman, J. Chem. Phys. **90**, 5651 (1989); S. W. Rick, D. L. Leitner, J. D. Doll, D. L. Freeman, and D. D. Frantz, J. Chem. Phys. **95**, 6658 (1991).

[2] C. Predescu, D. Sabo, J. D. Doll, and D. L. Freeman, J. Chem. Phys. **119**, 12 119 (2003); D. Sabo, C. Predescu, J. D. Doll, and D. L. Freeman, *ibid.* **121**, 856 (2004).

[3] C. Predescu, P. A. Frantsuzov, and V. A. Mandelshtam, J. Chem. Phys. **122**, 154305 (2005).

[4] C. Predescu, Phys. Rev. E **71**, 045701(R) (2005).

[5] P. Frantsuzov, A. Neumaier, and V. A. Mandelshtam, Chem. Phys. Lett. **381**, 117 (2003).

[6] P. Frantsuzov and V. A. Mandelshtam, J. Chem. Phys. **121**, 9247 (2004).

[7] J. P. Neirotti, F. Calvo, D. L. Freeman, and J. D. Doll, J. Chem. Phys. **112**, 10 340 (2000); F. Calvo, J. P. Neirotti, D. L. Freeman, and J. D. Doll, J. Chem. Phys. **112**, 10 350 (2000).

[8] R. H. Swendsen and J.-S. Wang, Phys. Rev. Lett. **57**, 2607 (1986).

[9] C. J. Geyer, in *Computing Science and Statistics: Proceedings of the 23rd Symposium on the Interface*, edited by E. K. Keramidas (Interface Foundation, Fairfax Station, 1991), p. 156.

[10] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983).

[11] The Cambridge Cluster Database, http://www-wales.ch.cam.ac.uk/CCD.html.

[12] J. A. Northby, J. Chem. Phys. **87**, 6166 (1987).

[13] J. P. K. Doye, D. J. Wales, and R. S. Berry, J. Chem. Phys. **103**, 4234 (1995).

[14] R. H. Leary, J. Global Optim. **11**, 35 (1997).

[15] D. J. Wales and J. P. K. Doye, J. Phys. Chem. A **101**, 5111 (1997).

[16] J. P. K. Doye, M. A. Miller, and D. J. Wales, J. Chem. Phys. **111**, 8417 (1999).

[17] F. Calvo and J. P. K. Doye, Phys. Rev. E **63**, 010902(R) (2001).

[18] D. D. Frantz, J. Chem. Phys. **115**, 6136 (2001).

[19] P. A. Frantsuzov and V. A. Mandelshtam, Phys. Rev. E **72**, 037102 (2005).

[20] J. P. K. Doye and F. Calvo, J. Chem. Phys. **116**, 8307 (2002).

[21] H. L. Davis, J. Jellinek, and R. S. Berry, J. Chem. Phys. **86**, 6456 (1987); T. L. Beck, J. Jellinek, and R. S. Berry, J. Chem. Phys. **87**, 545 (1987).

[22] F. Calvo, J. P. K. Doye, and D. J. Wales, J. Chem. Phys. **114**, 7312 (2001).

[23] G. A. Breaux, C. M. Neal, B. Cao, and M. F. Jarrold, Phys. Rev. Lett. **94**, 173401 (2005).