Quantum mechanics and the structure of noble-gas clusters

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The importance of quantum mechanics for the thermal behaviour of Argon clusters with special respect to phase transitions is investigated applying a Path-Integral Monte-Carlo (PIMC) method. Results for the small-angle neutron scattering function (SANS) for various cluster sizes and temperatures are presented.

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Introduction

In the investigation of molecules and clusters, the quantum effects arising from the motion of the atoms as quantum constituents of the system are expected to be very small and thus generally neglected. The wave functions have little overlap and the uncertainty in space is smaller than the interatomic distances. Because of the comparatively weak and soft binding of noble-gas atoms, for noble-gas clusters one should expect more extended atomic wave-functions and a higher importance of quantum contributions such as the groundstate energy. The quantum effects should be most important at a temperature where the spatial uncertainty is comparable to the statistical motion and the number of thermally accessible states is not too high. Here we want to study these quantum effects and their temperature dependence specifically for Argon-clusters and compare the results to classical ones.

So far, noble-gas clusters have been investigated by best-single-cluster approximations, Molecular Dynamics (MD) [1, 2], and classical Monte Carlo (MC) [3, 4, 2] simulations. Special attention has been directed to phase transitions of those clusters with the idea that the structure of the cluster is also important for its stability. Generally, the transitions are less sharp than in infinite systems but smeared out over some temperature range. Here we will specifically investigate an isomerization transition of $\text{Ar}_6$ because here it is easy to survey what happens on the microscopic scale.

The method

The multiparticle quantum statistics is reformulated in a pseudoclassical configuration space, assigning to every particle a "path" through this space along a closed imaginary "time"-axis. Statistical averages are calculated by integrating over the paths with a weight function $e^{-S/\hbar}$, S being the classical action of the path:

$$Z = \int D\psi(\tau) \exp \left\{ -\frac{\hbar}{\beta} \int_0^\beta d\tau (V(\psi(\tau)) + \frac{1}{2} m \dot{\psi}^2(\tau)) \right\}$$

(1)

where $D\psi(\tau)$ is running over all imaginable closed paths in configuration space of length $\hbar \beta$. The idea in applying this formalism is that for a system, for which quantum mechanics is not essential, the path space can be approximated by a few "time slices" and the remaining finite-dimensional integral can be calculated by a Metropolis-MC-algorithm [6]. (Note that in the limit of only one "time slice" the kinetic term of the action integral disappears and the classical configuration integral remains.) For the realization, a modification is necessary because the direct method of varying the path step-by-step causes extremely poor convergence. The configurational and kinetic energy terms must be decoupled by Fourier-transformation of the paths in the time-direction to allow the variation of the Fourier-components with different step sizes, reflecting their relative importance.

With this Path-Integral MC-algorithm we investigated the thermal behavior of Ar-clusters applying free
boundary conditions (no constraining potential was used). For the atomic interaction we took a standard Lennard-Jones potential with parameters \( \sigma = 3.405 \text{ Å}, \\ \varepsilon = 10.3 \text{ meV} \) (120 K) and a mass of 40 amu. For investigations of the \( \text{Ar}_n \) isomerization, we used around \( 10^6 \) iterations; when the cluster is dominated by only one structure, many fewer cycles are necessary to obtain reproducible results.

As information about the structure of the clusters and as connection to experimental work, we calculate the small angle elastic neutron scattering (SANS) function. Structure determination with neutron scattering gives directly the regions in which the nuclei move due to their thermal motion and not their convolution with the density distribution of core electrons as in the X-ray case. In addition, in experiments like those done by Oberthür et al. [8] at the D11 of the ILL Grenoble, cluster growth may be observed directly. For neutral noble-gas clusters the scattering function \( I(q) = 4\pi \sin \theta / \lambda \), calculated here from the pair correlation function \( g(r) \) out of the PIMC simulation, is

\[
I(q) = 4\pi \int g(r) \frac{\sin(qr)}{qr} r^2 dr. \tag{2}
\]

**Results of the calculations**

In the low temperature region, the quantum effects are expected to be most important because the zero-point energy is a large fraction of the total binding energy and prevents the cluster-atoms from taking full advantage of potential minima in configuration space. In this sense, it is somewhat in analogy with thermal energy at higher temperature. For the clusters investigated (Ar\(_6\) and Ar\(_{13}\)), the zero point energy lowers the binding energy by 10–15% and corresponds thus to thermal energies at \( \approx 15 \text{ K} \). On the other hand, with increasing temperature its influence decreases; above 30 K quantum effects cannot be observed in binding energies or in scattering functions.

The scattering function of an ensemble of \( \text{Ar}_6 \) clusters calculated by PIMC shows a shifting of maxima and amplitudes of about 10% at temperatures between 8.5 K and 12.5 K (Fig. 1). For clusters of this size, the shifting causes significant changes in both their internal structure and their shape. This indicates that there is some transition of the \( \text{Ar}_6 \)-cluster between these temperatures. The distinct structure in the region of high \( q \) demonstrates that the cluster geometry is dominated by few configurations. As it is seen from Fig. 2, there is a correction by quantum mechanics (Q) to the classical calculation (C) in the exact atomic position, but not in the overall shape (low momenta).

The ensemble of the \( \text{Ar}_{13} \)-clusters has a very well defined icosahedral structure below its phase transition (Fig. 3) while it looks amorphous above. The two maxima between 3 Å\(^{-1}\) and 4 Å\(^{-1}\) merge to one broadened one. Similar "strong" and amorphous icosahedral structures have been found by Cargill [9] in X-ray scattering experiments with the amorphous metals.