

Quantum mechanics and the structure of noble-gas clusters ¹

G. Franke and J. Schulte

Fachbereich Physik, Universität Oldenburg
D-2900 Oldenburg, FRG

Abstract

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

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isomerization transition of Ar₆ 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:

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

where $\mathcal{D}y(\tau)$ 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 $\sigma = 3.405\text{\AA}$, $\epsilon = 10.3\text{meV}$ (120 K) and a mass of 40 amu. For investigations of the Ar₆ 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 $I(q)$, $q = 4\pi \frac{\sin(qr)}{\lambda}$, calculated here from the pair correlation function $g(r)$ out of the PIMC simulation, is

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

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 ≈ 15 Kelvin. 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 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

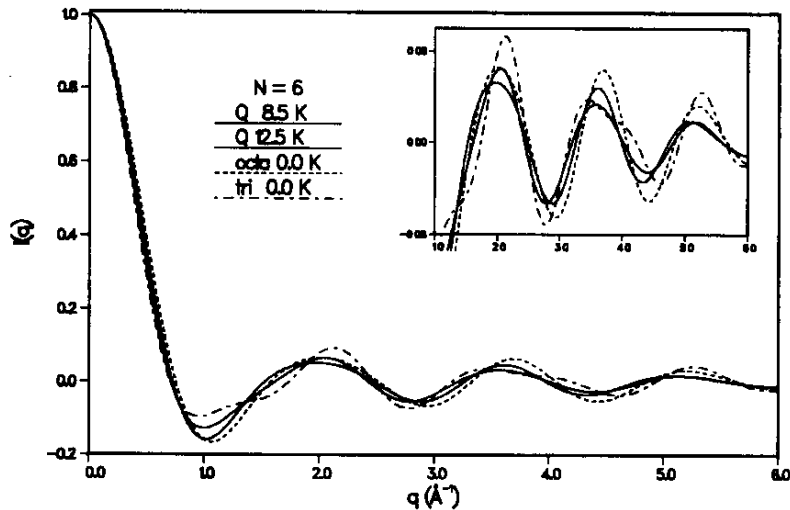


Figure 1: Scattering function of Ar_6 calculated by PIMC.

significant changes in both their internal structure and their shape. This indicates that there is some transition of the 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 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 \AA^{-1} and 4 \AA^{-1} merge to one broadened one. Similiar "strong" and amorphous icosahedral structures have been found by Cargill [9] in X-ray scattering experiments with the amorphous metals Pd-Si and Au-Si. Fig. 4 shows that quantum mechanical calculation (PIMC) yields observable corrections to the internal cluster structure (as we have proven up to temperatures of some 30 Kelvin), but leaves the cluster-shapes unchanged.

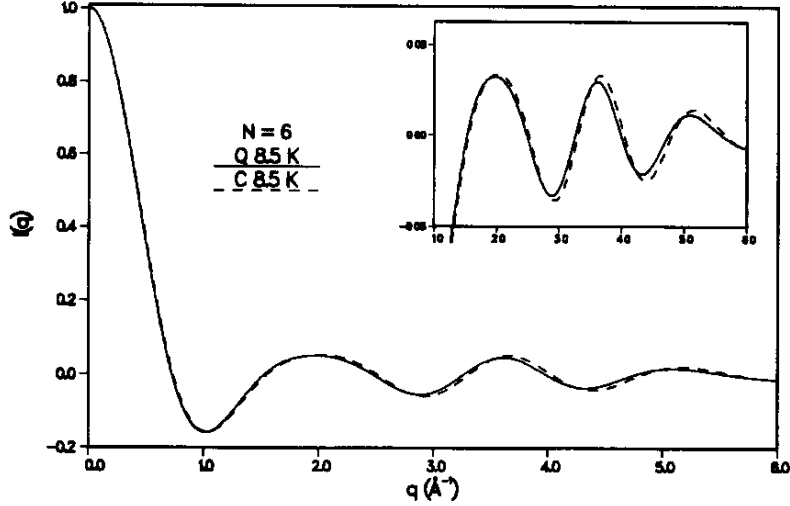


Figure 2: Scattering function of Ar_6 from classical (C) and PIMC (Q) calculations.

The two transitions observed in the calculations have different characteristics: while the Ar_{13} transition behaves very solid/liquid-like (in accordance to recent investigations [3,2]) in the sense that above the transition temperature the cluster looks amorphous, for Ar_6 at the transition only one configuration (built up of three tetrahedra) becomes important in addition to the octahedral ground-state structure. The SANS-functions for these structures are plotted in Fig. 1; their importance is confirmed by investigations of the pair correlation function and viewing single configurations produced in the MC-process. [7]

In the temperature range of the Ar_{13} -”melting” at ≈ 35 K, quantum mechanical corrections are not relevant, but also for Ar_6 we were not able to recognize an influence of quantum mechanics on the transition temperature with the precision of our calculations and a resolution of 0.5 Kelvin.

Discussion

In this section, we want to discuss the different characters of transitions occurring for Ar_6 and Ar_{13} . In the first case, in the transition region only two distinct configurations are relevant: the octahedron and the tri-tetrahedron. If we consider only these two (meta)stable states assuming that the volume of reachable phase space around them is equal, we can roughly estimate the transition temperature T_t . At T_t , the probabilities of finding the cluster in one of the two states are equal:

$$I_{\text{oct}} e^{-\frac{E_{\text{oct}}}{kT_t}} = I_{\text{tt}} e^{-\frac{E_{\text{oct}} + \Delta E}{kT_t}} \Rightarrow kT_t = \frac{\Delta E}{\log \frac{I_{\text{tt}}}{I_{\text{oct}}}} \quad (3)$$

Where $\Delta E = 0.41\epsilon = k \times 47K$ is the potential energy difference between the structures and I_{oct} , I_{tt} are the numbers of possible isomers of octahedron, and tri-tetrahedron, respectively. To determine them, we first ”divide” by permutations

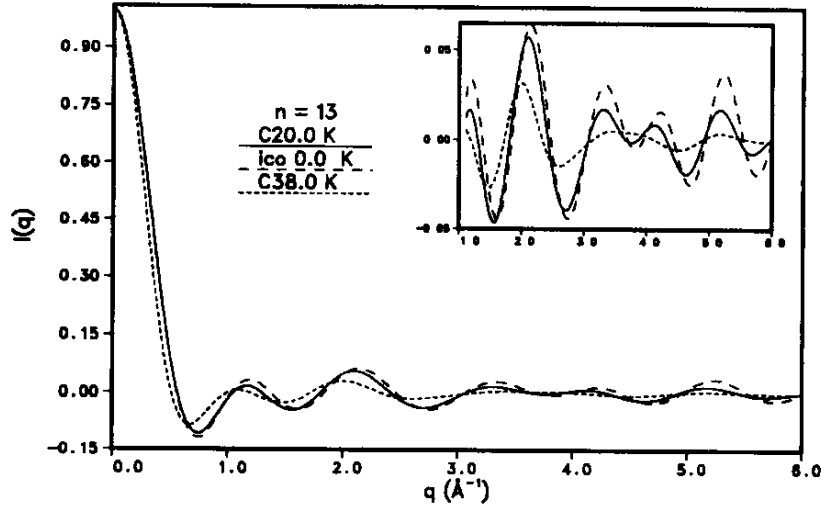


Figure 3: Scattering function of Ar_{13} from classical calculations.

and (continuous) rotations because they are common symmetries for all kinds of structures. Rotations that are equivalent to permutations — i.e. rotations which map the structure onto itself — have then been considered doubly. Although both the octahedron and tri-tetrahedron are unique structures, the ratio $\frac{I_{\text{tr}}}{I_{\text{oct}}}$ equals $\frac{24}{2} = 12$ because the order of rotational symmetry groups of the bodies are 24 (rotational subgroup of the octahedron-group) for the first and 2 (one 180° -axis perpendicular to the central pair-axis) for the second one. This yields a transition temperature of $T_t \approx 19\text{K}$. Compared to the simulation results, the temperature is overestimated by this simple model a factor of ≈ 1.8 . Probably, this is due to the higher mobility of the atoms of the tri-tetrahedron; for example the outer ones may move around the central pair.

Although this model allows only rough estimations of the transition characteristics, it should be useful for comparison of the behaviour of different clusters. Applying it to Ar_{13} , it is less clear from the simulation data which metastable configurations are important. Good candidates are only structures which completely break the icosahedral symmetry of order 60. Therefore we calculated the transition temperatures for a set of clusters obtained from the icosahedron by picking one or two atoms from the surface and placing them on top of it elsewhere. Distinguishing whether the moved particles are neighbouring or not, the model yields 3 very similar transition temperatures in the range of 62 – 67 Kelvin.

Compared to the experimental data cited above, we also have an overestimation of the temperatures of about 1.8. But besides this factor, we recognize the following fact: in contrast to Ar_6 , where just one isomerization takes place at T_t , here we have at least three overlapping transitions in a range of $\frac{5\text{K}}{1.8} = 3\text{K}$. (Probably also more complex metastable states are thinkable but there it becomes difficult to survey what happens.) From the viewpoint of isomerizations, this fact is the reason for the sudden arising of liquid-like behaviour of Ar_{13} which led Berry et

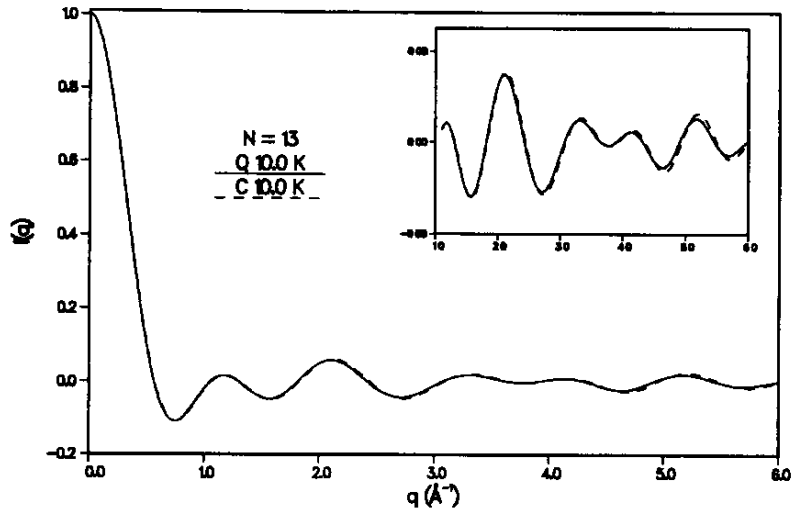


Figure 4: Scattering function of Ar_{13} from classical (C) and PIMC (Q) calculations.

al. to the introduction of a phenomenological melting-model for clusters [5]. Our interpretation implies that the melting-like behaviour of Ar_{13} is accidental; having more distinct transition temperatures for the most easily achieved states would lead to a more complex temperature dependence.

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