

Quantum Mechanics and Phase Transitions in Small Noble-Gas Clusters

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Abstract

The quantum-statistical properties of Argon clusters are calculated applying a Path-Integral Monte-Carlo (PIMC) method. Results for pair correlation functions and kinetic- and configurational energy expectations for various cluster sizes and temperatures are presented. Physical phenomena such as ground- state kinetic energy and quantum admixture of different atomic configurations are studied and experiences with the method are given. In particular, the relation between metastable cluster states and phase transitions is discussed.

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1 Introduction

Molecular clusters have been intensely studied in recent years, both experimentally and theoretically [1]. They serve as a bridge between up to now quite different fields of physics, such as the few possible space bulk crystal structures vs. the infinity of possible surface-relaxed configurations of atoms in a cluster of finite size or the thermally sharp phase transitions of bulk matter vs. the smooth changes of order parameters in a cluster [2]. In particular, noble-gas clusters have been investigated by best-single-cluster (BSC) approximations [3-7], Molecular Dynamics (MD) [8-13] and classical Monte Carlo (MC) [14-17,10] simulations. Special attention has been directed to phase transitions of those clusters with the idea, that the cluster's structure is also important for its stability. Generally, they are less sharp than in infinite systems but smeared out over some temperature range. Berry et al. introduced a phenomenological model [18] assigning unequal transition temperatures to freezing and melting of the cluster leading to a coexistence region of solid and liquid phases. Here, we will compare these predictions with own results obtained from quantum mechanical MC-calculations and discuss the concept.

The quantum mechanics of the electrons in metal clusters has been extensively studied, for a nice recent account of the present status see [19]. There the particles are completely delocalized fermions, the Fermi energy being much higher than any barrier between different configurations and quantum statistic effects are governed by the Fermi statistics [20]. On the other hand for the atoms as quantum constituents of the clusters in general one does expect only minor quantum effects, since they are much heavier and their wave functions have little overlap - the uncertainty in space is smaller than the interatomic distances. The kinetic energy is much smaller than the barrier to the position of any neighbouring atom, so that they are expected to oscillate only locally about their fixed positions in space and the difference between classical and quantum statistics will be small.

Here we want to study specifically quantum effects of noble gas clusters, with the idea, that here, if ever, quantum effects should show up. Because of the comparatively weak and soft binding, one should expect more extended atomic wave-functions, relatively larger kinetic energies compared to the binding, and even quantum contributions such as the kinetic groundstate energy. To the extreme, it is well known, that for a non-rotating two-body Lennard-Jones system of noble gas atoms there are only 2-4 bound states found and the zero-point energy is a large fraction of the total binding energy. The quantum effects, however, should become less important for higher temperatures as quasiclassical approximations will serve the region of larger numbers of accessible states.

The usual method to calculate quantummechanically straightforward a multiparticle system would be to solve the many-particle Schrödinger equation numerically, that is quantum-MD. Even though one may skip the

quantum statistics of the particles the numerics get quickly out of hand with growing particle numbers.

A different approach studies a cluster in thermal equilibrium. There, in making use of the assumption that the classical dynamics may still be no bad approximation it has turned out wise to move to the Path-Integral formulation of the Quantum Dynamics. It is more suitable to be combined with MC-algorithms (Path-Integral Monte-Carlo, PIMC) than the wave function formalism [21]. Especially from Lattice gauge-theory calculations PIMC has proved itself to be a powerful tool for the quantum simulation of bound systems. Thus Freeman and Doll adjusted and applied it for free-energy calculations for Argon-clusters [22,23].

For the setup of a quantum-mechanical calculation of cluster properties, a physical model for the interactions between noble gas atoms is required. Many different suggestions have been made and discussed in the past: Pure two-body interaction models such as Lennard-Jones (6-12) or more sophisticated ones [24] are easy to handle but not in all cases sufficient physicswise. For example, the crystal structure of frozen noble gases cannot be explained by pure two-particle forces. Therefore several three- (or more-) body interactions have been proposed [25,26].

For ionized clusters - which can more easily be investigated experimentally - an additional charge-dipole interaction is present. Haberland [27] gave arguments for the reliability of the dimer model, where the positive charge is assumed to be localized on one dimer of atoms within the cluster. Detailed quantum-chemical calculations on the forces in this LJ model have been done by Böhmer and Peyerimhoff [28]. For simplicity, we will constrain ourselves to pure LJ-Forces, allowing a comparison to recent results and serving as a reference for future investigations of other interaction models.

2 The Algorithm

The multiparticle quantum statistics is reformulated in a pseudoclassical configuration space, assigning to any particle a "path" through this space along a closed imaginary "time"-axis of length $\hbar\beta$ [29]. Statistical averages are calculated by integrating over the paths with a weight function $e^{-S/\hbar}$, S being the classical action of the path. For example

$$O = O(x) \Rightarrow \langle O \rangle = \frac{1}{Z} \int \mathcal{D}y(\tau) O(y) e^{-S} \quad (1)$$

with the real exponent

$$S[y(\tau)] = \int_0^{\hbar\beta} d\tau (V(y(\tau)) + \frac{1}{2} m \dot{y}(\tau)^2) \quad (2)$$

where $\mathcal{D}y(\tau)$ is running over all imaginable closed paths in configuration space of length $\hbar\beta$. For p-dependent operators, the functional limit used in eq. (1) is not unique but nevertheless the practical calculation of averages is not problematic.

The idea in applying this formalism is that for problems which behave close to a classical system. (which would be described by an integral over paths of length zero, i.e. a classical configuration integral) the path space can be approximated by a few "time slices".

The computation of the functional integral (1) can be performed after splitting the paths into m discrete steps at "times" τ_k , so that a finite- (i.e. $3Nm$) dimensional integral remains. For the calculation of the "moments" $O(y)$ resp. $O(\dot{y})$ of the weight function $e^{-S/\hbar}$, the Metropolis-algorithm [30] is a convenient method because no explicit normalization by the partition function is required.

In realization of this algorithm, problems arise from the necessity to choose the random step from one path to the next one in a way that optimizes convergence: The direct method of varying the particle-coordinates $y_i(\tau_k)$ of each time step was found to cause extremely poor convergence. The reason is, that the changes of the configurational and the kinetic terms due to the statistical motion in one time-step are not in the same order of magnitude. Especially at high temperature, the dynamics of the stochastic MC-process is determined only by the second one and the change of configurations becomes very slow. To avoid this problem, one has to decouple potential and kinetic energies by Fourier-transformation of the coordinate-step in time-direction. Then the change in configurational energy is mainly determined by the zero-component as the classical part, that does not contribute to the kinetic part. Thus one can choose different step sizes for the Fourier-components, reflecting their relative importance.

Adjustment of the Method

Experimentally as well as theoretically. Argon clusters have been investigated most intensely of all noble gas clusters in the past: thus, for better comparison to results of other methods, in the present work we apply PIMC

specifically to Argon clusters. For the atomic interaction we take here 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.

To obtain relevant information about the geometrical structure of the cluster, one has to define mean values of quantities that are invariant under symmetry transformations such as rotation and particle exchange which do not influence the physical properties of the system. Furthermore individual configurations that contribute to mean values are in general not representative for the phase space in total. Finally, mean values of individual particle-coordinates are meaningless in the framework of multiconfiguration statistics. As a simple quantity to contain geometrical information we investigate the real-space pair correlation function:

$$\Gamma(r) = \left\langle \frac{2}{N(N-1)} \sum_{i<j}^N \delta(|x_i - x_j| - r) \right\rangle \quad (3)$$

where the x_i are particle positions. The function gives the probability distribution for the 2-particle distance r to be realized in the cluster [15]. The positions of the peaks of it reflect very sensitively the most probable "crystallographic" structure of the cluster. Their width provides a measure for its thermal and quantum-mechanical uncertainty.

The nearest-neighbour distance - i.e. the position of the first peak - reflects only the minimum of the two-particle potential. But already the next-nearest-neighbour distance - the second peak - can be used as "fingerprint" of geometric structures. For some of the most important classes of configurations, we remind of the values (in terms of the nearest-neighbour distance $R_0 = \sqrt[3]{2}\sigma$):

- fcc and octahedron: $\sqrt{2} = 1.41$
- multi-tetrahedron: $\sqrt{\frac{8}{3}} = 1.63$ and $\frac{5}{3} = 1.67$
- pentagonal rings and icosahedron: 1.62 .

Also the distinctness of the peak structure of the correlation function allows to discuss the mobility of the cluster's particles and thus serves for investigations of the phase transitions in small clusters. Other quantities of interest are - for the discussion of stability problems - the mean value and variance of the potential and kinetic energy. The deviation of the last one from its fixed classical value of $\frac{3}{2}NkT$ may provides a measure for the temperature dependent role of quantum effects.

All the technical parameters used for the calculations have been checked to have no influence on the results. They are adjusted in order to optimize the rate of convergence of the Metropolis-procedure. In particular, the following quantities are important:

- The relative weights of the Fourier-components turned out to depend on temperature and cluster size and are adjusted in order to cause equal rates of Metropolis-rejections. Test variations in the range of one order of magnitude did not influence the results.
- The size of one MC-Step was chosen such that the portion of rejections was about 20-25%.
- Apart from transition regions, about 20,000 iterations (i.e. 250,000 different configurations for $N = 13$) preceded by the same number of "warming up" cycles obtained reproducible results that also did not change under continuation of the calculations. Where several strongly separated configurations become important, 10-50 times more iterations are required. Starting points used are pieces of a fcc-lattice or of an icosahedron.
- The approximation of the action-integral turned out to be good enough when the distances between the net points are about $1/(40K \times k_B)$ or less, that is, the number of Fourier-components has to be greater than $40/T[K]$. This implies that above 40 Kelvin, quantum effects are no longer observable.

The $N = 13$ cluster provides a good subject for a test because its icosahedral structure is very compact and is known to be the most stable one. Starting from a cuboctahedral configuration, also compact and metastable ($3.6\epsilon = 36.7\text{meV}$ above groundstate), after 5000 iterations with PIMC at 5 K the characteristic fcc-peak in the correlation function has already completely disappeared and the icosahedral pattern is reproduced.

3 Structural Transitions and Melting

While at zero temperature the microcrystalline structure of the clusters is well defined by the minimum of potential energy, for increasing temperature one expects two types of thermal effects:

- In addition to the quantum uncertainty, the cluster geometry becomes softened by local oscillations of the particles around their classical equilibrium positions.
- At higher temperature, the admixture of essentially different configurations should come in. We will discuss in what sense this can be considered as "melting".

As a good example for the first type, fig. 1 shows the correlation functions (normalized to equal maximum) of the Ar_{13} -cluster for a set of temperatures. As expected, below 35 K one observes the characteristic broadening

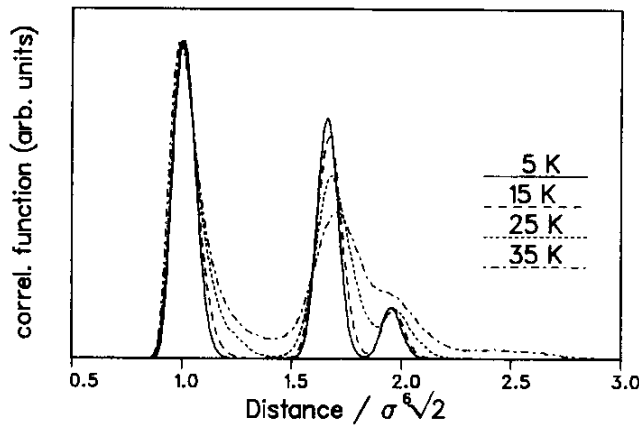


Figure 1: Correlation Functions for Ar_{13}

of the peaks with T which is due to the increasing local oscillations. Additionally the gaps between the peaks are more and more filled. This means that also configurations deviating from the icosahedral pattern increasingly contribute to the thermal averages: deformations of the cluster (possibly global shape oscillations) take place but the "topological" structure remains.

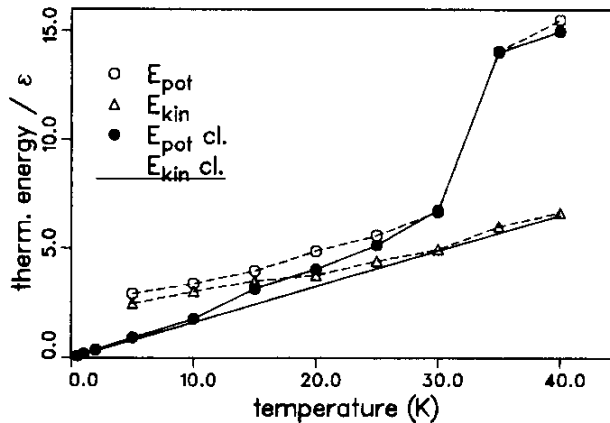


Figure 2: Thermal Energies for Ar_{13} (above $E_{min} = -44.3\epsilon$)

The icosahedral structure is remaining as the dominating one below 35 K because competing metastable structures have too high energy and thus low thermal probability. This fact is also reflected by fig. 2. There, the kinetic energy of the system, and the total potential energy above the (icosahedral) maximum binding energy of -44.3ϵ (-457meV), of classical and quantum mechanical calculations are shown. In the region of low temperature where the thermal vibrations are small, the two-body potential is approximately harmonic so that the Virial Theorem with exponent 2 — as expected — is approximately fulfilled yielding equal configurational

and kinetic energy. Also for higher temperatures, the potential and kinetic energy curves run nearly parallel indicating that nonlocal motion plays a minor role.

For Ar_{13} , nonlocal motion becomes relevant at temperatures above 35 K. In the correlation function, a tail arises, indicating that at least one particle has left the shell of the icosahedron to walk on top of it. Because of the missing atom(s), the motion of the remaining ones is less constrained and therefore the characteristic next-nearest-neighbour pattern disappears. These results on the dissolution of the icosahedral structure are qualitatively the same as obtained in other (classical) MC-calculations [17,10]; even the temperature where it takes place is in the same range (although we made no attempt to determine it exactly). (The interpretation in terms of "melting" will be discussed below.) MD-calculations on the same subject exhibit a qualitatively different behaviour [8]. There the $T(E)$ curves exhibit a "melting loop" and a change of slope at a sharp (and quite low) temperature with a very similar behaviour of different-sized clusters. This is due to the fact, that in MD-simulations, thermal occupation probabilities play no role and thus the influence of metastable isomers begins immediately when the total energy becomes higher than the energy barrier. The system's residence time in them is long because of the reduced particle velocity at higher potential. In contrast, in thermodynamic calculations it is short because of the lower energy barrier for return to groundstate.

While the behaviour of Ar_{13} is very much melting-like in the sense that above the transition temperature no particular structure can be recognized, we will now examine another type of structural transition of a cluster, Ar_6 . The icosahedron is a unique and very stable structure staying stable also at higher temperature whereas the groundstate of Ar_6 is also highly symmetric but much less stable. Fig. 3 shows the temperature dependent transition of the correlation function of Ar_6 . The single next-nearest-neighbour peak observed at 5

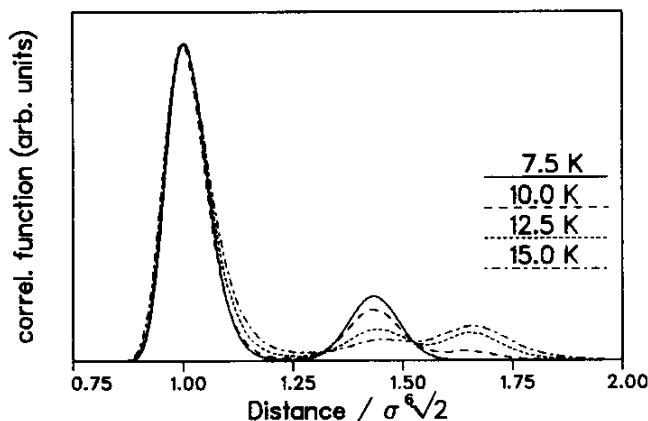


Figure 3: Correlation Functions for Ar_6

Kelvin corresponds to a purely octahedral structure with lowest potential energy. At higher temperature, an additional peak appears (also well localized) due to increasing admixture of isomers built up of three tetrahedra (see fig. 4). The relative importance of the octahedron decreases and above 20 Kelvin, the peak is no longer

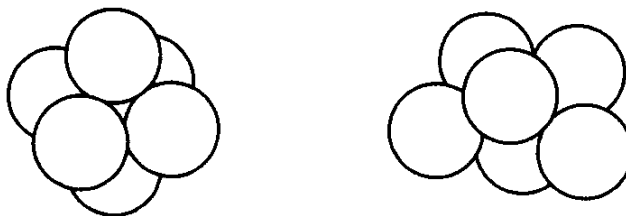


Figure 4: Most stable isomers of Ar_6 : left — octahedron ($E_{pot} = -12.7\epsilon$), right — tri-tetrahedron ($E_{pot} = -12.3\epsilon$)

observable. The washed-out curves for higher temperatures correspond to the relative freedom of the outer atoms of the tri-tetrahedron to move around the inner pair. The thermal energies plotted in fig. 5 also confirm that above 10 K the reachable configuration space gets larger leading to an increased slope of $E(T)$, i.e. to a specific heat maximum.

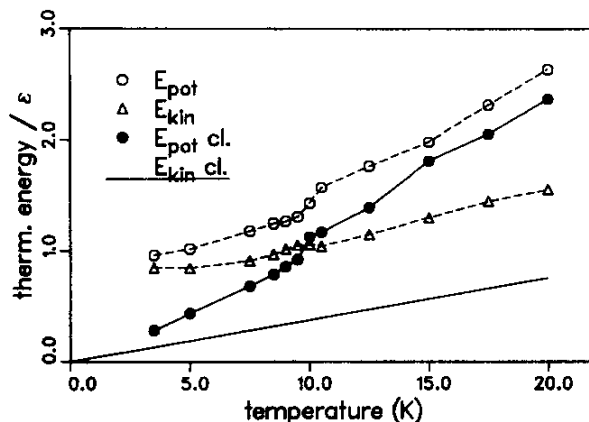


Figure 5: Thermal Energy of Ar_6 (above $E_{\min} = -12.7\epsilon$)

4 Discussion

The $E(T)$ curves for Ar_6 and Ar_{13} both indicate a specific heat peak at some temperature and thus a phase transition of the cluster. With respect to the correlation function, the Ar_{13} cluster has a very well-defined structure below a transition temperature while it looks amorphous above it. This fact led in recent works [15] to the interpretation of this phase transition as "melting" of the cluster. Based on a phenomenological model, Berry, Jellinek and Natanson [18] introduce unequal melting and freezing temperatures which leave space for a coexistence region of the two phases. MC-simulation data are interpreted in terms of this model assigning the attributes "solid" and "liquid" to configurations produced during the program runs [10]. In contrast, we want to discuss this phenomenon in terms of structural transitions, using the case of Ar_6 as a prototype.

From the correlation function, it is obvious that for Ar_6 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 and -range. At the transition temperature T_t , the probabilities of finding the cluster in one of the two states are equal:

$$I_{\text{oct}} e^{-\frac{E_{\text{oct}}}{kT_t}} = I_{\text{tt}} e^{-\frac{E_{\text{oct}} + \Delta E}{kT_t}} \Rightarrow kT_t = \frac{\Delta E}{\log \frac{I_{\text{tt}}}{I_{\text{oct}}}} \quad (4)$$

Where $\Delta E = 0.41\epsilon = k \times 47K$ is the potential energy difference between the structures and $I_{\text{oct}}, I_{\text{tt}}$ are the numbers of possible isomers of octahedron, and tri-tetrahedron, respectively. To determine them, we first "divide" by permutations 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 octahedron and tri-tetrahedron are unique structures, the ratio $\frac{I_{\text{tt}}}{I_{\text{oct}}}$ equals $\frac{2^4}{2} = 12$ because the order of the bodies' rotational symmetry groups 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 $T_t \approx 19K$. 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.

Defining the transition region as the temperature range, where the relative probability of the structures increases from e^{-1} to e^{+1} , with the same arguments we get

$$k\Delta T_t = \frac{2\Delta E}{\log^2 \frac{I_{\text{oct}}}{I_{\text{tt}}} + 1}, \text{ here: } \Delta T_t \approx 13K \quad (5)$$

which seems also to be overestimated by the same factor when compared to the calculated correlation function.

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. Compact ones like fcc- (cuboctahedron) or hcp-based play no role because the energy shift is high (cuboctahedron: $\Delta E = 3.6\epsilon$) and the number of isomers is low. 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. Moving one particle, the energy shift is $\approx 3\epsilon$ and the effective number of isomers is $\frac{1}{I_{\text{iso}}} = 60 \times 4$ yielding $T_t \approx 63K$ and $\Delta T_t \approx 22K$. Moving 2 particles, energy shift as well as isomer numbers depend on whether they are neighbouring or not. We get for neighbouring \rightarrow neighbouring: $T_t \approx 62K$, $\Delta T_t \approx 16K$; neighbouring \rightarrow distinct: $T_t \approx 67K$, $\Delta T_t \approx 8K$; distinct \rightarrow distinct: $T_t \approx 71K$, $\Delta T_t \approx 7K$.

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 structural transition takes place at T_t , here we have at least three overlapping transitions in a range of $\frac{5K}{1.8} = 3K$. (Probably also more complex metastable states are thinkable but there it becomes difficult to survey what happens.) From the viewpoint of structural transitions, this fact is the reason for the sudden occurrence of liquid-like behaviour of Ar_{13} : the motion between four competing structures is complex enough to look liquid-like and the transition's temperature range is small because the probabilities have to be added. This interpretation implies, that the melting-like behaviour of Ar_{13} is accidental; having more distinct transition temperatures for the most easy states would lead to a more complex temperature dependence.

The Role of Quantum Effects

It turned out that the simulation results up to ≈ 30 Kelvin from classical and quantum calculations differ Kelvin for the energy values as well as for the correlation function. Obviously the quantum effects are most important for low temperature where the zero-point energy inhibits the reduction of the cluster structure to the classical state of minimal energy. In the cases investigated, it tends to a value of 10-15% of the total binding energy which is in the order of magnitude of thermal energies at 15 K. Due to the virial theorem, the potential and kinetic shares are approximately equal.

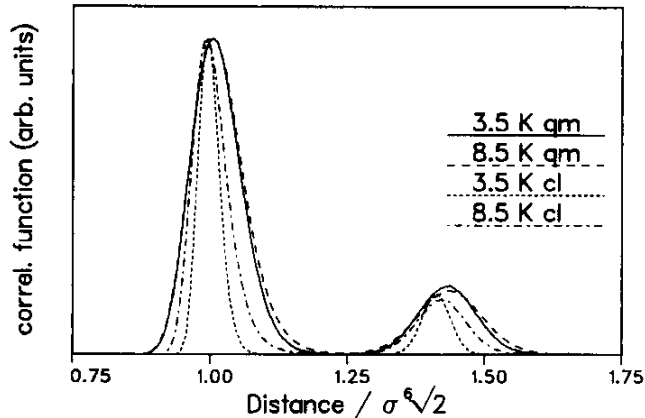


Figure 6: Correlation Functions for Ar_6 from classical and quantum calculations

The quantum mechanical correlation functions for low temperature are much more "smeared out" than the classical ones (see fig. 6). The quantum uncertainty of the particle positions looks somewhat like the thermal broadening at higher temperature. Thus, one could expect an influence of quantum effects on low-lying transition temperatures because the cluster cannot fully "exploit" its low potential below the transition. In fact, we were not able to recognize a quantum-shift of the transition temperature of Ar_6 with a resolution of 0.5 K; this effect seems to be very small. But with respect to the energy, the transition in the quantum case is less sharp than in the classical case due to the permanent influence of zero-point motion. We conclude that quantum effects act somewhat like the finite size of the system leading to a less sharp transition behaviour.

5 Entropy and Boundary Conditions

In a rigid thermodynamical sense, free clusters (no external pressure, at fixed temperature) are only metastable objects because the part of phase space where the atoms form a rarefied, almost noninteracting gas is infinite while the binding energy of the unified cluster is only finite. In the MC calculations this is reflected by the absence of a constraining potential that leads to the eventual evaporation of particles after a relaxation-time proportional to $e^{-\beta\epsilon}$, ϵ being the evaporation energy. Thus, results of the calculations are to be interpreted in

the sense of a simulation of the metastable cluster-state for times short compared to the evaporation relaxation-time.

The importance of entropy for cluster structure and -stability is obvious and one can see its acting for example at structural transitions. Nevertheless in the framework of free clusters, it is not well defined from "first principles" and one has to choose a more pragmatic definition, taking into account only the bound cluster-states and not the continuum. For the method of calculation by integrating $TdS = dE$ from a high-temperature reference point (pure gas phase) down to T as for example used by Freeman and Doll [22], the introduction of an artificial "constraining potential" is essential and its arbitrary shape may have some influence on the results. To start the integration from a low-temperature reference point ($T = 0$) should be possible also for free clusters but would require reliable results for extremely low temperatures which can hardly be provided by PIMC. We expect that the entropy would be higher for clusters for which no compact (e.g. icosahedral) structure is available and therefore the $N = 13$ stability would be lowered when considering the free energy $F = E - TS$, as compared to the energy consideration — especially at higher temperatures.

6 Outlook

By using the Path-Integral formulation of quantum mechanics, it was possible to calculate the quantum effects even in these quite complex multiparticle systems with no restriction to the phase space. Quantum effects proved to contribute to the mobility of the individual atoms (starting from the zero-point kinetic energy) and to the superposition of different configurations. Generally, the isolation of quantum effects is difficult because thermal and quantum effects act in the same direction.

PIMC seems to be a useful method for the investigation of multiparticle systems of up to 25-30 constituents if the interactions are not too complicated. The LJ-potential is mathematically the most simple one and it will be interesting to compare the results presented here to those obtained by using more sophisticated interaction models. We plan to investigate the role of three-body terms and that of polarization and the built-in dimer for charged clusters [31].

Acknowledgements

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