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Thermodynamic properties of small rare gas clusters by path integral Monte Carlo simulations: a preliminary study

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Abstract. A strategy for reducing the risk of non-ergodic simulations in Monte Carlo calculations of the thermodynamic properties of clusters is discussed with the support of some examples. The results obtained attest the significance of the approach for the low-temperature regime, as non-ergodic sampling of potential energy surfaces is a particularly insidious occurrence. Fourier path integral Monte Carlo techniques for taking into account quantum effects are adopted, in conjunction with suitable tricks for improving the procedure reliability. Applications are restricted to Lennard-Jones clusters of rare-gas systems.

Keywords: Cluster – Path integral – Monte Carlo

Introduction

Due to the dominance of surface effects, it is known that clusters behave in a very different way from bulk matter, with the consequence that new properties, not displayed by extended solids, come to light. This means that the picture of a cluster as a fragment of a solid, with the same structure, is an unacceptable oversimplification. Understanding the differences in behavior of nanosystems with respect to bulk materials is an important challenge of for present-day research that has motivated cluster studies for years, and with successful future perspectives. Unlike bulk matter, physical properties (thermodynamic, electrical) of most clusters exhibit very irregular dependence on size, in particular on the number *n* of monomers involved. These anomalies determine the well-known "magic number" effect [1]. In view of these peculiarities, numerous applications of nanoaggregates are expected, in a variety of technological branches (from PC memories, to the medical sector, to fine chemical catalysis). Indeed, the need to know the behavior of nano-structures in detail and the requirement to provide a rationale for controlling their size and structure have contributed to focus our own interest in this area of research.

In principle, the spatial structure of a cluster is essentially a result deducible from the inspection of the (very complex) Potential Energy Surface (PES) produced by the interactions between the monomers in the clusters [2]. Each minimum in this surface is associated with a possible isomeric structure of the cluster. At sufficiently low temperatures, the lifetime of an isomer is long enough that we can study the path and the transition states connecting the various minima, although their statistical weights for thermodynamic properties can be very different. Obviously, the PES availability is a prerequisite for theoretical work on clusters. For a system involving a large number *n* of particles, obtaining this Born-Oppenheimer (BO) hypersurface (possibly in interpolated analytical form [3]) is a difficult and generally very expensive task, because it demands in principle that the quantum-mechanical electronic problem, with clamped nuclei in a sufficiently large number of geometries, has been explored and accurately solved. Only after the PES of the system is known does it become possible to begin a computational statistico-mechanical approach [2, 4] for the calculation of thermodynamic properties.

The careful and efficient exploration of the PES, an especially critical step for systems involving a great number of atoms and for simulations at low temperature, constitutes perhaps the principal goal toward which we focused our interest. Indeed, if the sampling of the PES leaves us unable to assign correct statistical weights to the various PES regions, then we will be not be able to avoid systematic errors caused by quasi-ergodicity phenomena in the results. This problem, an almost regular occurrence in finite-length Monte Carlo

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simulations, arises most frequently when the PES contains regions characterized by very low transition probability between each other, with high risk of sampling confined to only one of these regions. The problem is especially insidious because the resulting quasi-ergodic simulation can exhibit rapid convergence and low asymptotic variance, but with an error of definite sign (a systematic error that does not decrease as the walk number increases), a clear indication of procedural breakdown. Moreover, the failure due to quasi-ergodicity can be very marked in simulations performed at low temperature, because PES basins not associated with the global minimum-energy cluster geometry (and, therefore, not very important statistically) are preferentially sampled. This is a problem of particular significance in the case of clusters with high particle number, and in simulations started with a spatial distribution wrongly guessed as that of global minimum.

The main intent of this work is to test a strategy (that we call "Growth") that allows us to reach the global minimum-energy basin of the n-particle cluster in the warm-up stage, using knowledge of the geometrical minimum structure of the (n−1)-particle cluster in a recursive manner. In this way, the possibility of performing simulations on structures with minima that are only presumed (which occurs when using an initial random spatial disposition of the particles or, worse, when using a structure derived from bulk properties) is much reduced.

We apply the method to simple systems that show the quasi-ergodicity phenomenon, demonstrating how we can ensure ergodic sampling. With the aid of other simple tricks, the method can be extended to systems of greater complexity. Our applications will be limited to simple Ar and Ne clusters, investigated in earlier studies [5, 6, 7, 8].

Method

All of the thermodynamic properties of a system consisting of an arbitrary number n of particles can be obtained from the knowledge of the canonical density operator:

$$\hat{p}(\beta) = \exp\left[-\beta\hat{H}\right] = \exp\left[-\beta\left(\hat{K} + \hat{V}\right)\right] \tag{1}$$

where $\hat{H} = \hat{K} + \hat{V}$ is the Hamiltonian operator of the system, the sum of the kinetic energy $\hat{K}$ and the potential energy $\hat{V}$ operators, and $\beta = (k_B T)^{-1}$ is the temperature parameter, k_B being the Boltzmann constant. $\hat{V} = V(r_1, r_2, ..., r_n)$ depends on the n particle positions $\{r_1, r_2, \ldots, r_n\}$, and defines a hypersurface geometrically (PES). For the applications considered in this work, $V(r_1, r_2, \ldots, r_n)$ is the result of the Born-Oppenheimer solution of the electronic problem, and $\hat{K}$ is the nuclear kinetic energy. Considering the time evolution operator of the system, $\hat{U}(t) \equiv \exp\left[-\frac{it}{\hbar}\hat{H}\right]$, it is easily recognized that $\hat{p}(\beta) = \hat{U}(-i\hbar\beta)$ (in other words the canonical density operator is formally the evolution operator at imaginary values of time, t).

The expectation value of any property F can be derived as follows:

$$\langle F\rangle = \frac{Tr\left(\hat{p}\hat{f}\right)}{Tr\hat{p}} \tag{2}$$

where $\hat{f}$ is the quantum-mechanical operator corresponding to the property F. In the path integral approach suggested by Feynman [9, 10, 11, 12, 13], the traces appearing in Eq. 2 are usefully expressed in the coordinate representation. If the operator $\hat{f}$ is diagonal in such representation, we obtain the following compact result:

$$\langle F\rangle = \frac{\int d^{3n}r\langle r|\exp\left(-\beta\hat{H}\right)|r\rangle f(r)}{\int d^{3n}r\langle r|\exp\left(-\beta\hat{H}\right)|r\rangle} \tag{3}$$

involving multidimensional integrals extended to the overall configuration space.

There are two principal methods of evaluating the diagonal matrix elements $\langle r|\exp\left(-\beta\hat{H}\right)|r\rangle$, interpretable as closed path-integrals. In the first one, the path-integral is discretized by subdividing each path covered in the imaginary time β into a large number N of stages of small "duration" β/N, where the approximation:

$$\exp\left(-\beta\hat{H}/N\right) \simeq \left[\exp\left(-\beta\hat{K}/N\right)\right]\left[\exp\left(-\beta\hat{V}/N\right)\right] \tag{4}$$

can be assumed to hold. The resulting multidimensional integral for $\langle F\rangle$ is then computed using Monte Carlo (M.C.) methods [4, 11, 13]. The second way of approaching the evaluation of $\langle F\rangle$ makes use of a Fourier representation of the paths, through the expansion of each of them in a sine Fourier series about the straight line reference trajectory [2, 6, 14, 15]. This alternative procedure leads to the expression:

$$\langle f\rangle = \frac{\int\left(\prod_{k=1}^{k_{\max}}\prod_{i=1}^{3n} da_{k,i}\right) d^{3n}r\, p_{k_{\max}}(r,a) f(r,a)}{\int\left(\prod_{k=1}^{k_{\max}}\prod_{i=1}^{3n} da_{k,i}\right) d^{3n}r\, p_{k_{\max}}(r,a)}$$

Here a is a compact notation for all of the Fourier expansion coefficients $a_{k,i}$, in analogy to the r employed for all of the $3n$ configuration coordinates. In practice the Fourier representation is truncated at a given $k_{\max}$ for each of the $3n$ spatial variables (depending on the accuracy required) and the resulting expression is again evaluated by MC techniques (FPIMC approach, from Fourier Path Integral Monte Carlo, is the acronym most frequently used). Both procedures described above clearly give rise to an increment of the effective number of degrees of freedom (for example they become $3n(k_{\max} + 1)$ in the second case), a consequence of the necessity to adequately treat the involved path integrals so as to pick up the embedded quantum effects [11, 12, 13, 14]. Such increment of the dimensionality of the integrals involved legitimates the use of MC methods [16], which are not be very susceptible to dimensionality problems.

The formulation adopted in this section provides average values of properties according to the statistical mechanics canonical ensemble. In the case of macroscopic systems, all of the representative ensembles (canonical, microcanonical, and so on) are to be considered equivalent, due to the typically small energy fluctuations involved. In the case of clusters, the role of these fluctuations can be important, influencing the choice of the statistical ensemble. In view of the interests explicitly declared in this paper, namely the behavior of thermodynamic properties as temperature changes, the most suitable choice seems to be the canonical ensemble [11].Running into problems associated with inaccurate sampling is a common occurrence for clusters involving many units, or for simulations at very low temperature, and they result in poor results from the MC simulations due to quasi-ergodicity effects. The warm-up period (sometimes called thermalization), a necessary preliminary activity for all Monte Carlo calculations carried out using the Metropolis algorithm [17], is a stage during which we proceed to sample the configuration space without data accumulation. During warm-up, the spatial disposition of the cluster atoms is changing in search of an energetically stable geometrical structure, which is statistically very important, bearing in mind the final goal (thermodynamic properties). Therefore, the warm-up period should lead to increased accuracy of MC calculations, and to independent results for the initial spatial disposition of the cluster particles. The duration of this period, however, risks becoming very long and time expensive, especially if the minimum-energy structure is unknown and the initial particle disposition is random or is that characterizing bulk matter. A great number of steps are actually required, in general, to reach the global minimum-energy basin (or an energy basin in communication with it, at the low temperature of the simulation) from a random initial disposition. This number increases dramatically as the particle number becomes large, particularly at low temperatures, which is why in such conditions a good warm-up for clusters involving more than 15 particles is difficult to perform. According to the "Growth" strategy mentioned in the preceding section, in the procedure tested in this work the most stable structure of the *n*-particle cluster is built up, starting from the (*n*-1)-particle cluster stable structure, in a recursive way. The new particle is located a certain distance from the ($n-1$)-particle cluster and added to it according to dynamics simulating a nucleation process. Only a modest number of MC steps are required for the particle to reach its proper location in the cluster while the other particles rearrange themselves in order to give rise to the global minimum-energy structure.

For larger clusters (with more than 20 atoms) the strategy described can be improved by keeping an eye on the energy changes resulting from different approach directions (equatorial or axial) for the added particle in the first stage of the warm-up.The efficiency of the "Growth" procedure can also be improved through its coupling with the so-called Parallel Tempering (PT) method [18], a clever approach devised to reduce quasi-ergodicity risks by increasing the probability of sampling configuration basins by configurational exchanges through two parallel simulations that proceed at different temperatures. Obviously, the higher the simulation temperature, the broader the PES explored. The exchange periodically attempted between configurations generated in the course of the higher temperature simulation and that at the temperature of interest can occasionally be accepted, allowing the exploration of PES basins of otherwise difficult sampling.

A really efficient PT procedure would actually require several simulations at different, increasing temperatures. In this work we used PT involving two simulations, with some changes with respect to the original suggestion. Actually, even though the two simulations run parallel, the one at the temperature T of interest involves quantum calculations in terms of path integrals. The auxiliary simulation at the higher temperature T_j is carried out in terms of the faster and simpler classical algorithm. Only at the trial exchange moment, with an established frequency (in this work every 100–500 MC steps), the configurational energy at T_j proposed for the exchange is obtained via path integrals and is used to evaluate the acceptance. In this way the detailed balance condition is satisfied. In fact, if Z is the configurational integral, for the joint density we find that the low temperature walk is at configuration r and the high temperature walk is at configuration r':

$$\rho_2(r,r') = Z^{-1}e^{-\beta V(r)}e^{-\beta_3 V(r')}$$

where $V(r)$ is the potential energy of the system in the configuration r. The ratio of the conditional transition probabilities is therefore:

$$\frac{K(r \rightarrow r', r' \rightarrow r)}{K(r' \rightarrow r, r \rightarrow r')} = \exp\left[-\left(\beta - \beta_j\right)\left(V(r')\right)\right]$$

With the following choice of the acceptance criterion:

$$acc(r_0 \rightarrow r_n) = \min\left[1, \exp\left[-\left(\beta - \beta_j\right)\left(V(r_n) - V(r_0)\right)\right]\right]$$

at the moment of the configuration exchange (with $V(r_n), V(r_0)$ correctly calculated by path integrals), the detailed balance condition is satisfied [17]:

$$\rho(r_0)K(r_0 \rightarrow r_n) = \rho(r_n)K(r_n \rightarrow r_0)$$

so that the random walk visits the configuration space with a probability proportional to the density $\rho(r)$.

The net result of the procedure described is a considerable time saving (simulations carried out in classical terms involve negligible time cost compared to those where quantum effects via path integrals are taken into account), without significant differences in answers from the PT procedure based on two parallel quantum simulations.

It is worth noting that in the course of this work we have tested the utility of a few additional procedures, between them the J-walking method [19] (an approach which is similar to PT) and Tsallis statistics [20, 21]. As far as application of these statistics are concerned, their extension to the FPIMC context is still insufficiently explored, although from preliminary investigations the approach does not look entirely satisfying.

The applications discussed in this paper (see next section) are limited to a schematic PES built in terms of simple pair interactions represented by standard Lennard-Jones model. This simple potential appears adequate to describe rare-gas clusters. Our successive considerations refer to the following PES:

$$V(r) = 4\varepsilon\sum_{i<j}^{n}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + V_{\mathrm{C}}$$

$$V_{\mathrm{C}} = \sum_{i=1}^{n}\left(\frac{|r_i - R_{\mathrm{C.M.}}|}{R_{\mathrm{C}}}\right)^{20}$$

where V_{C} is a constraining potential energy acting to reflect particles reaching a coordinate near $|r - R_{\mathrm{C.M.}}|$ near R_{C}, and is essentially zero for bound particles [18]. The codes elaborated at our laboratory are sufficiently flexible to allow easy extension to other interaction models.

Results

Prototype systems

The first results we are going to present concern the Ar clusters Ar_{15} and Ar_{19} (the latter a "magic" cluster). Our choice of small Ar aggregates is motivated mainly by their relative simplicity, largely due to a quantal behavior that is not too strong. The following considerations, however, are also valid for other monomeric species and are most significant for clusters involving lighter particles (such as Ne and H_2), where the research into methods and tricks to reduce the computational costs becomes not only useful but imperative.

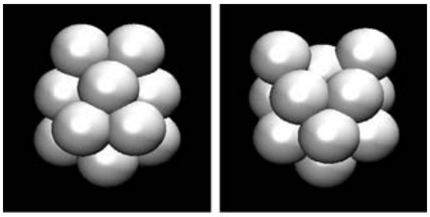
To reach the global minimum-energy structure of an aggregate involving 15 atoms, starting from an initial random disposition of the particles in the space, 5×10^6 MC steps are needed on average at 1–1.5 K. On the other hand, by "Growth" strategy, 10^5 steps are enough. An inadequate warm-up stage can produce a great waste of computational time: the number of steps can be even greater than that needed for the simulation itself. For Ar_{15}, in fact, it is possible to have 0.1% error in the energy with only 10^6 MC steps if the simulation starts from an adequate, energetically stable, geometrical structure of the cluster.

Now we can move on to present the results of the simulations concerning Ar_{15}. The most stable thermodynamic structure of this cluster arises from an icosahedral model of growth. In this case, however, we are confronted with two possible isomers, according to whether the couple of atoms added to the icosahedral core of the magic Ar_{13} cluster are respectively near neighbors (structure I) or not (structure II), as shown in the Fig. 1. The two isomers are related to two different potential wells present in the cluster PES, and have different energies. A third isomer (structure III), characterized by a non-icosahedral geometry, displays some stability at sufficiently low temperatures, and becomes statistically meaningful at higher temperatures. During a simulation at high temperature ($T > 15$ K) the random walk samples all important configurations; however, at low temperature it can remain trapped in a potential well all of the time. The structure assumed by the cluster during a simulation can be understood by monitoring the order parameter Q_4 [18], because its value is strictly dependent on the geometry. In particular $Q_4 \simeq 0$ for icosahedral structures and $Q_4 \simeq 0.19$ for f.c.c. structures.

In Table 1 Ar_{15} energies for different outcomes of the warm-up at very low temperatures are compared with the cluster global minimum-energy, while Fig. 2 shows how Q_4 changes during different warm-up runs.

As the particle number in the cluster increases, a lot of complications arise as a consequence of the proliferation of possible metastable isomers, whose structures are harder to resolve into that of greatest stability. This remark can be easily verified considering the case of Ar_{19}. For this cluster, the "Growth" strategy offers a short cut to obtaining the global minimum-energy structure, that is the icosahedral one. Figure 3 shows how the parameter Q_4 changes during a standard warm-up stage of Ar_{19} and during a "Growth" of Ar_{18}. In the first case, we observe changes in Q_4 between 0.10 and 0.19, while in a warm-up run by "Growth", Q_4 remains steady around zero, an indication of an icosahedrical-type structure, the most stable one.

It is interesting to note the differences between the "Growth" strategy implemented in our procedure and the older algorithm used by Hoare [22]. The calculation of thermodynamic properties of nanostructures suggested in [22] involves a factorization of the canonical partition function with respect to vibrational, rotational and translational modes of the most stable cluster structure. The method is sufficiently accurate at very low temperatures, but is at variance with MC simulations at temperatures where several phases can coexist. In fact, the statistical weight of the various possible structures is actually ignored. To determine the minimum-energy structure, Hoare builds a tree of the possible isomers, on the basis of fundamental structures (tetrahedral, octahedral and icosahedral) for seed-clusters of four, six and seven atoms respectively, locating additional atoms at all possible packing vertices at the surface. The successive optimization of the distinct structures by steepest descent algorithm allows us to discern the most stable isomer, but at the cost of a very laborious procedure,



(a) isomer I (b) isomer II

(c) isomerIII

Fig. 1. Isomers of the Ar_{15} cluster. Their relative energies are reported in Table 1

Table 1. Relative energy results from simulations with insufficiently long warm-up stages and with initial particle dispositions as in Fig. 1. The simulations remain trapped in the P.E.S. basins relative to each initial isomer. U_0 is the exact internal energy for the most stable cluster isomer. The calculations are performed by a warm-up of 10^6 steps and a M.C. walk of 3×10^6 steps. The warm-up is inadequate for addressing the cluster in its more stable icosahedral structure, whose statistical weight is dominant at very low temperature. Using warm-up of "Growth" type, the global minimum-energy structure and correct energy are easily reached

$k_BT/\epsilon = 0.0125$	$\langle Q_4 \rangle$	U/U_0
I isomer	0.0088	I
II isomer	0.0075	0.970 ± 0.005
III isomer	0.082	0.960 ± 0.005
Structure by "Growth"	0.0087	$I \pm 0.005$

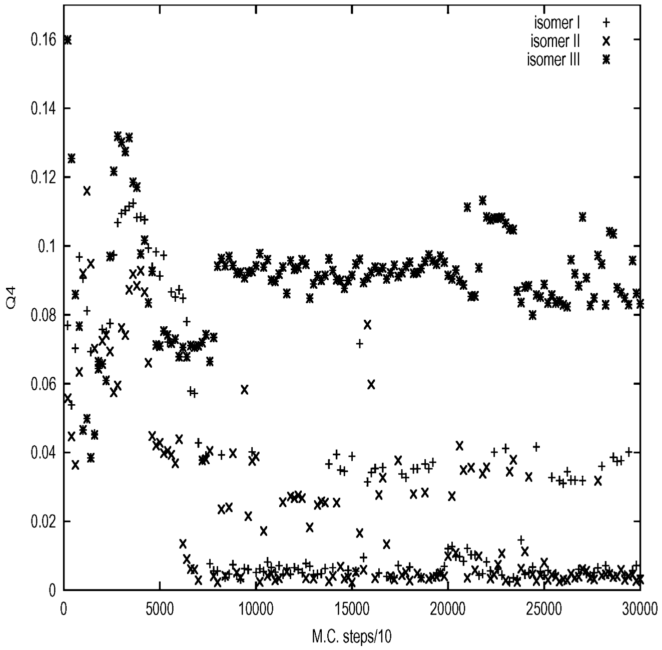


Fig. 2. Isomeric structures of the cluster Ar_{15}, as viewed through the order parameter Q_4. Each isomer has a different distinguishing value of Q_4 during the simulation. In particular, the isomer III (the most energetic one) assumes values very different from 0

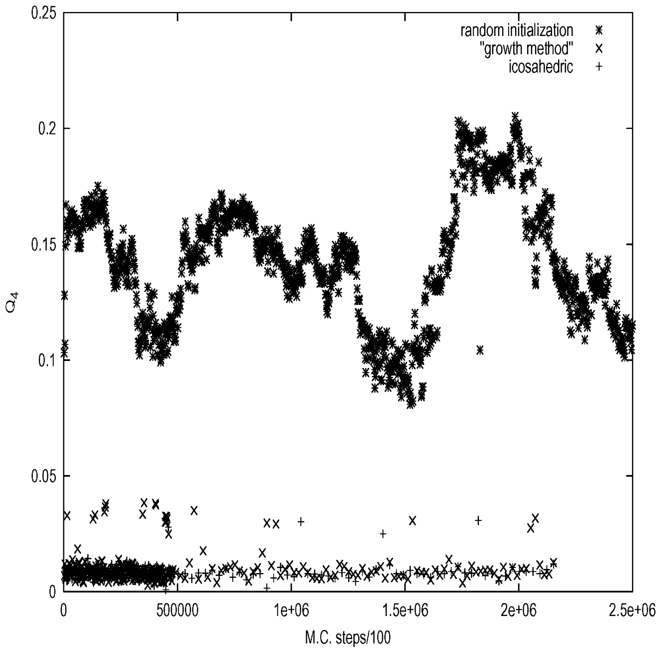


Fig. 3. Behavior of the order parameter Q_4 during a simulation for Ar_{19}. The figure shows Q_4 values from warm-up in terms of random initial disposition of the atoms, and from "Growth" warm-up. The latter is associated with a icosahedral-type structure, that of greatest thermodynamic stability

particularly when a great number of possible isomers are involved due to the cluster size. Our method, though not so systematic, takes advantage of the power of the MC simulations, where at low temperature the cluster is automatically pushed toward its energetically most stable structure, corresponding in some sense with the statistical path forced by the density function. Further developments of our approach, however, could profit to a noticeable extent by ideas put forward in [22] (for example the determination of distinct growth schemes on the basis of the different inertia tensors involved).

Thermodynamic properties of clusters

The considerations of this subsection will be limited to a few thermodynamic properties: internal energy, heat capacity at constant volume, and Gibbs free energy of formation from the monomers. The internal energy U plays a primary role. After this property has been obtained, in fact, all of the remaining thermodynamic functions follow readily (in principle, at least). Therefore, the molar Gibbs free energy of formation can be derived according to [6]:

$$\frac{\Delta G_{\mathrm{m}}^{0}}{RT} = (1-n)\ln\left(\frac{\rho^{0}}{k_{\mathrm{B}}T}\right) - \ln\frac{Q(n, V_{\mathrm{m}}, T)}{V_{\mathrm{m}}} + \ln\left(\frac{2\pi m k_{\mathrm{B}}T}{h^{2}}\right)^{3n/2}$$

where:

$$\ln Q(n, V_{\mathrm{m}}, T) - \ln Q(n, V_{\mathrm{m}}, T_{\infty}) = \frac{1}{k_{\mathrm{B}}}\int_{T_{\infty}}^{T}\frac{U(n, V_{\mathrm{m}}, T')dT'}{T'^{2}} \tag{5}$$

The evaluation of the canonical partition function $Q(n,V_{\mathrm{m}},T)$ from Eq. 5 demonstrates that all thermodynamic properties can be derived through knowledge of the internal energy.

The free energy of formation is clearly a very important quantity for several reasons. Predictions about cluster stability, depending on temperature and particle number, can in fact be made on the basis of $\Delta G_{\mathrm{m}}^{0}$ data. The same data are also of noticeable help in nucleation studies (according to the homogeneous steady-state nucleation theory [23]), particularly in relation to growth models of nanosystems.

A rather critical point concerning the evaluation of thermodynamic properties, internal energy in particular, is associated with the choice of the best estimator for the property investigated. As far as the internal energy is concerned, we used two main estimators (referred to as the T-method and V-method respectively) with different convergence behaviors and computational time demand. Even though the role and properties of these estimators have been widely discussed [15], we performed preliminary tests on the two alternatives in order to get direct experience about their convergence characteristics, in particular the dependence on temperature and the truncation parameter $k_{\max}$ introduced in FPIMC simulations. In order to optimize the convergence characteristics, we used Partial Averaging [6, 24], a technique that allows us to take (approximately) into account the coefficients ignored due to the truncation of the Fourier representation of the involved path integrals. For both estimators and Partial Averaging, it is right to point out that the subject is still a very contentious one, as attested by recent contributions [15, 25, 26]. All of this deserves considerable attention in view of applications to come.

In analogy to the internal energy, the evaluation of the heat capacity at constant volume, C_{V}, can be carried out by resorting to different estimators. In this regard, we will briefly mention that the virial estimator [7] involves a greater computational time demand, in exchange for more accuracy and regular convergence to the exact value (at low temperatures) as $k_{\max}$ increases.

Our simulations, as already mentioned, concern Ar and Ne clusters, about which a vast literature over the last 20 years can be reported. Looking at the quantity:

$$\overline{\Delta G}(n,p,T) = G(n,p,T) - G(n-1,p,T) - G(1,p,T) \tag{6}$$

the free energy of formation of the n-particle cluster from the (n−1)-particle [6], it is possible to find a first justification of the "magic number" effect in the formation process of the cluster (see Fig. 4). From an experimental point of view, "magic" numbers can be defined with reference to the presence of local peaks in mass spectra. A local minimum of a certain value, in the plot of $\overline{\Delta G}(n, p, T)$ against the number n of monomers in the cluster, is associated with the presence of a "magic number". Looking at Fig. 4, we notice that the formation of Ar clusters containing 7, 13, and 19 atoms is a highly favored process.

Heat capacity calculations on Ne and Ar clusters also support the presence of peculiarities in the behavior of clusters, at variance with the regular changes exhibited by thermodynamic properties of bulk matter as temperature is varied. From this point of view, the "magic number" effect is clear too. The C_V versus temperature T plots display sharper phase change regions and higher peaks in the case of "magic clusters" compared to non-magic clusters. In Fig. 5, the plot shows the height of the C_V peak as the number n of particles in the cluster is varied. Ar clusters with $n = 19$ and $n = 13$ are magic not only with reference to the Gibbs free energy of formation but also to C_V.

It is very interesting to compare, as a function of T, the specific heat behavior of 13-atom clusters of Ar and Ne, as shown in Fig. 6. For this comparison it is convenient to work in terms of the reduced temperature, k_BT/ε, ε being the Lennard-Jones energy parameter for the specific atom involved. The plots exhibit similar shapes, with maxima located close to each other and rather dissimilar in value. Both curves display an initial

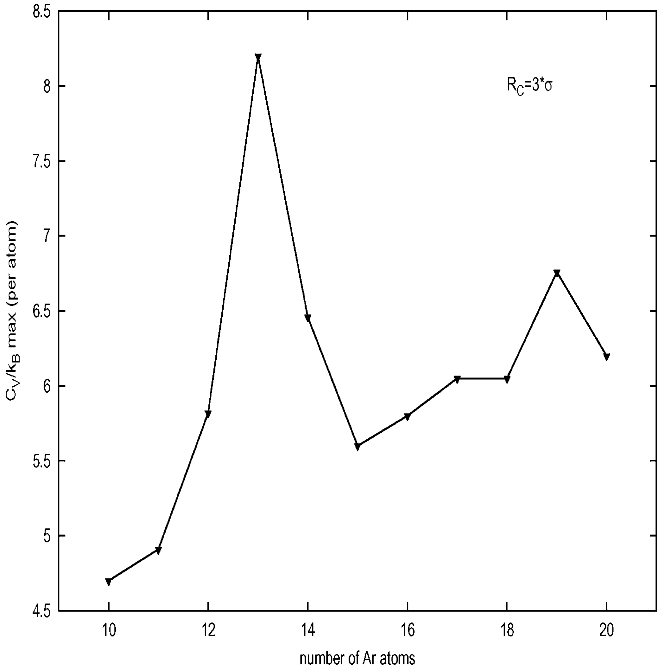


Fig. 5. $C_V(T)$ maximum peak as a function of number of particles in Ar clusters. The numbers $n = 13$, 19 are magic

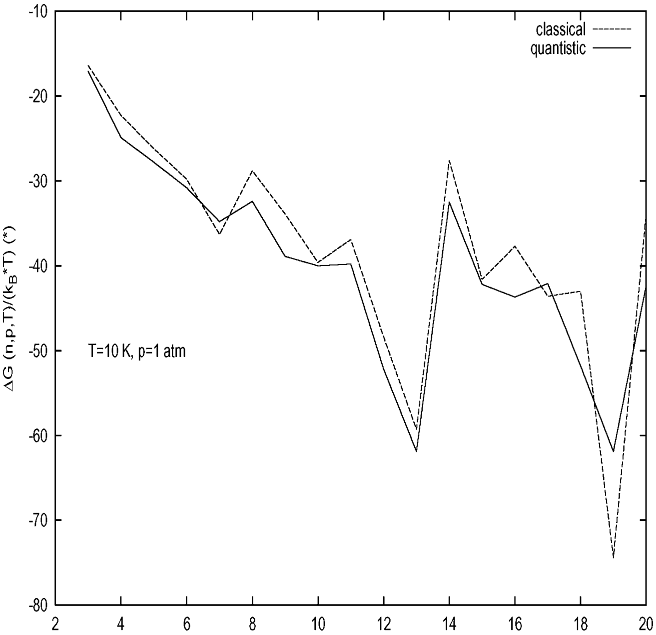


Fig. 4. $\overline{\Delta G}(n, p, T)$ behavior (Eq. 6) vs. number of atoms in clusters at $p = 1$ atm. Note the presence of "magic number" structure corresponding to the favorite formation of Ar_{13} and Ar_{17} (minima in the plots). A third minimum, less evident, corresponds to Ar_7 (magic, too)

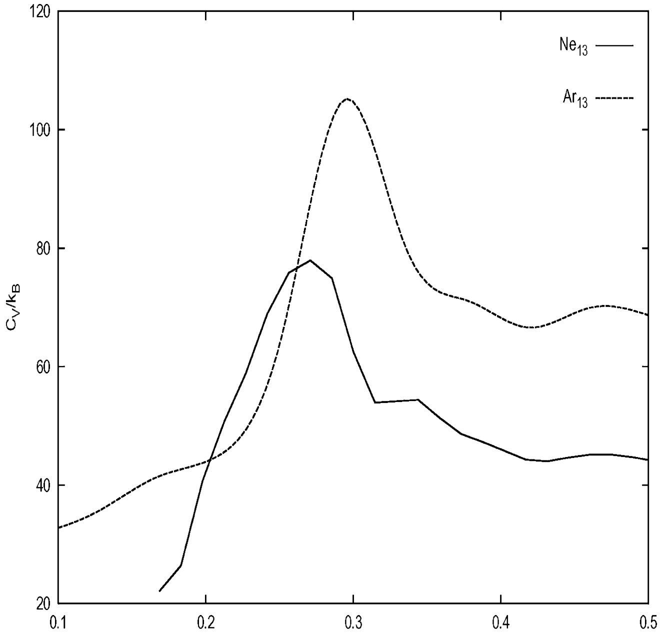


Fig. 6. Behavior of $C_V(T)$ vs. reduced temperature for Ar_{13} and Ne_{13} clusters. The curves display similar shapes, which is typical behavior for clusters modeled with pair additive Lennard-Jones potentials

zone (on the maximum left-hand side) where C_V increases, as a consequence of the possibility of exploring other regions of the PES. corresponding to different isomers. On the far right-hand side, C_V maintains a rather high value, due to the evaporation effect (one should note that the maximum is associated with the change from solid to liquid phase). A comparison of the same type as that presented in Fig. 6 can be found in [28]. In this regard, we limit ourselves to pointing out that our findings agree favorably with those of the latter reference, even though the methods adopted in the simulations are very different.

Conclusions

The exploitation of a strategy named "Growth" has been shown to be effective for exploring of the global minimum-energy structure of Lennard-Jones clusters,via FPIMC simulations, in critical situations (at low temperature). This method allows us to save a large amount of computational time and to avoid dangerous quasi-ergodicity effects during the calculation of thermodynamic properties. Quasi-ergodicity problems are especially insidious at low temperature, because in the absence of a good warm-up stage they can lead to simulations sampling PES configurational basins devoid of important statistical weight. The coupling of this strategy with P.T. gives the procedure further strength. It could be very interesting to improve P.T. according to recent ideas about the role of multiple "time step" MC [29].

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