

Molecular dynamics study of the Ag_6 cluster using an *ab initio* many-body model potential

I. L. Garzón, I. G. Kaplan, R. Santamaria, and O. Novaro

Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, México, D.F., 01000 México

(Received 24 September 1997; accepted 6 May 1998)

A general approach to construct a model potential with parameters fitted to *ab initio* energy surfaces, including many-body nonadditive effects, developed in our previous works is applied to the Ag_6 cluster. A molecular dynamics study of structural and dynamical properties of this cluster is performed using such a potential. Two new stable two-dimensional isomers with C_{2v} and C_{2h} symmetries are identified as local minima of the potential surface using the simulated quenching technique. An analysis of the thermal stability as a function of the cluster temperature reveals interesting features in the meltinglike transition of Ag_6 . A two-step isomerization phenomenon is observed: at temperatures around 300 K, the cluster structures fluctuate among two-dimensional isomers, at higher temperatures (500 K), fast transitions occur between two- and three-dimensional cluster configurations. The simulation was extended up to the cluster fragmentation which is observed through dimer evaporation. © 1998 American Institute of Physics.
[S0021-9606(98)52230-1]

I. INTRODUCTION

The study of physical and chemical properties of atomic and molecular clusters is a very active field of research nowadays. One of the main objectives is to understand the changes in the fundamental properties of materials as a function of size, evolving from isolated atoms or molecules to the bulk phase, through the use of appropriate descriptions of the interatomic interactions in such systems.¹⁻⁴ From a theoretical point of view, several approaches based on first principles⁵ and computer simulation⁶ methods have been implemented to study a variety of cluster properties.

Molecular dynamics (MD) is one of the most commonly used computer simulation techniques to study the structure and dynamics of clusters. However, it requires a reliable description of the interatomic forces of the systems under study. A lot of work has been performed using phenomenological pairwise interactions like the Lennard-Jones potential for rare-gas atom clusters,⁷ and the Coulomb plus Born-Mayer potentials for the ionic ones.⁸ Recently, a systematic study of the most stable cluster structures using a two-body Morse potential, for different ranges of interaction, was reported.⁹ To study covalent and metal clusters a more complex description is needed since they interact through angular-dependent and nonadditive forces. Several semiempirical *m*-body model potentials containing parameters fitted to bulk properties have been applied to the calculation of cluster properties giving questionable results in covalent¹⁰ and metal¹¹ systems. The nontransferability of bulk-derived model potentials to clusters is explained by the lower atomic coordination of the finite systems, which are characterized by a much higher surface to volume ratio than bulk materials.

Ab initio MD is an alternative approach to make simulation of clusters without using model potentials. The Car-Parrinello (CP) method,¹² which combines MD and density

functional theory (DFT), has been applied to calculate structural and dynamical properties of metal^{13,14} and semiconductor¹⁵ clusters. Other related *ab initio* MD schemes based on DFT,¹⁶ the Hartree-Fock method,¹⁷⁻²⁰ and generalized valence bond techniques,²¹ have also been used in the study of metal clusters. In general, *ab initio* MD methods provide accurate results on the structural and electronic properties of small clusters. However, the study of dynamical properties with an equivalent degree of accuracy requires significant computational resources.¹⁸⁻²⁰ Neglecting electron correlation and using fully optimized codes and parallel processing, simulation times of the order of 100 ps have been recently attained in dynamical studies of small lithium clusters.¹⁹

Another approach is to use model potentials fitted to *ab initio* data in classical MD simulation of clusters. The advantages of this strategy are that simulation times can be extended up to the nanosecond regime and many-electron systems like transition and noble metal clusters can be studied. Electron correlation effects can be introduced through the use of state-of-the-art *ab initio* results in the parameter fitting procedure. *Ab initio* model potentials were proposed by Clementi and co-workers^{22,23} and more recently used in liquid water simulations.²⁴ In cluster studies, a size-dependent *ab initio* model potential was constructed by Blaisten-Barojas and Khanna²⁵ for the prediction of stable geometries of Be_n clusters. Later, it was used in Monte Carlo²⁶ and MD²⁷ simulations of such systems. In metal surfaces and interfaces of NiAl crystals *ab initio* model potentials were recently developed by Cooper *et al.*²⁸

The thermal stability of clusters is one of the most interesting phenomenon to be studied in finite systems. One of the distinctions between molecules and clusters is based on the different mechanisms in which they dissipate thermal

energy. In a molecule, as thermal energy is transferred into the system, it passes directly from vibrational-rotational to dissociative states. In a cluster, thermal energy can be dissipated through several mechanisms: by cluster isomerization or melting, or by boiling off atoms (evaporation). From a theoretical point of view, detailed analysis of the thermal stability in transition and noble metal clusters (including such phenomena as isomerization, melting, premelting, surface melting and evaporation) have been done by classical MD simulations.^{29–37} Most of these studies were carried using semiempirical m -body model potentials with parameters fitted to experimental data of bulk systems like cohesive energy, nearest neighbor distances and elastic constants. In other studies, the parameters of the m -body potentials are fitted using *ab initio* and experimental data of both small clusters and bulk matter.^{30,33,38,39} Nevertheless, the applicability of such semiempirical potentials to the study of cluster properties is not evident. For example, the MD study of transition metal clusters using bulk and surface empirical potentials is ambiguous, making the calculated properties dependent upon the experimental data used for the parameter fitting.¹¹ The problem appears when bulk potentials, assuming a homogeneous distribution of electron density in the system, are used to calculate the binding or cohesion energy of clusters. For a correct study of the bonding and stability of finite systems, it is important to introduce the discrete nature of the electronic spectrum.⁴⁰ In other words, a description of the cluster bonding based on atomic and molecular conceptions is more appropriate to mimic the interactions in finite systems.

In this work, we used a general approach to construct an *ab initio* model potential including two-, three-, and four-body interaction terms based on a physically reliable expression for the cluster binding energy.^{41,42} Our objective is to show that a model potential based on the theory of intermolecular forces, which gives a more realistic representation of the different contributions to the bonding in metal clusters, can be successfully applied to a MD simulation study. Specifically, we investigate the structural changes that metal clusters undergo when their temperature is varied, using an accurate and reliable description of the m -body interactions. It should be noted that *ab initio* model potentials are also useful to understand the peculiarities of the electronic structure of the systems under study. In this respect, the information on the relative contribution of exchange and dispersion forces to the cluster stability, is of considerable interest to gain insight on the interplay between the electronic properties and geometric structures.

We illustrate the above approach by using an *ab initio* model potential for the study of the Ag_6 cluster. A knowledge of the physical properties of small silver clusters is of great interest in connection with technological applications as photographic⁴³ and catalytic⁴⁴ materials. Several theoretical studies on the cluster structure and electronic properties in the size range of $n \leq 9$, have been done using different quantum-mechanical methods.^{45–49} A dynamical study of the Ag_6 cluster as a function of temperature is of special interest due to the competition in stability of two- and three-dimensional isomers, corresponding to local minima of the

potential energy surface. Preliminary results of applying this approach to study some isomers of the Ag_6 cluster were published in Refs. 41,42. The plan of the paper is as follows:

Section II describes the procedure to construct the model potential and how to fit its parameters to *ab initio* data calculated by the nonlocal spin density (NLSD) method. In Sec. III we present the results of the MD simulation and give a discussion of them. A summary and the conclusions of this work are given in Sec. IV.

II. AB INITIO MODEL POTENTIAL

The *ab initio* model potential V developed in Refs. 41,42 includes two-, three- and four-body interaction energies: V_2 , V_3 and V_4 . Each of them consists of exchange and dispersion terms.⁵⁰ The reason for including many-body interaction terms into the model potential is based on theoretical studies of cluster stability.^{51–53} The inclusion of many-body terms is specially important if the model potential is fitted to *ab initio* calculated potential surfaces.

The expression of the three-body exchange energy was proposed in Ref. 54. For the four-body exchange energy a similar term was used. The analytical form of the dispersion terms was taken from perturbation theory up to fourth order. Thus, the *ab initio* model potential V as a function of the interatomic distances r_{ij} was taken in the following form:^{41,42}

$$V = V_2 + V_3 + V_4, \quad (1)$$

$$V_2 = \sum_{i < j}^n \left[A_2 \exp(-\alpha r_{ij}) - C_6 \frac{D_6(r_{ij})}{r_{ij}^6} - C_8 \frac{D_8(r_{ij})}{r_{ij}^8} - C_{10} \frac{D_{10}(r_{ij})}{r_{ij}^{10}} \right], \quad (2)$$

$$V_3 = \sum_{i < j < k}^n \left[A_3 \exp\left(-\gamma_3 \sum_{i < j}^{\{ijk\}} r_{ij}\right) + C_9 \frac{D_3(r_{ij})D_3(r_{ik})D_3(r_{jk})}{r_{ij}^3 r_{ik}^3 r_{jk}^3} \times (1 + 3 \cos \Theta_i \cos \Theta_j \cos \Theta_k) \right], \quad (3)$$

$$V_4 = \sum_{i < j < k < l}^n \left[A_4 \exp\left(-\gamma_4 \sum_{i < j}^{\{ijkl\}} r_{ij}\right) + C_{12} [f(ijkl)D(ijkl) + f(ijlk)D(ijlk) + f(ikjl)D(ikjl)] \right], \quad (4)$$

$$\begin{aligned}
f(ijkl) = & (r_{ij}r_{jk}r_{kl}r_{li})^{-3}[-1 + (\mathbf{u}_{ij} \cdot \mathbf{u}_{jk})^2 + (\mathbf{u}_{ij} \cdot \mathbf{u}_{kl})^2 \\
& + (\mathbf{u}_{ij} \cdot \mathbf{u}_{li})^2 + (\mathbf{u}_{jk} \cdot \mathbf{u}_{kl})^2 + (\mathbf{u}_{jk} \cdot \mathbf{u}_{li})^2 + (\mathbf{u}_{kl} \cdot \mathbf{u}_{li})^2 \\
& - 3(\mathbf{u}_{ij} \cdot \mathbf{u}_{jk})(\mathbf{u}_{jk} \cdot \mathbf{u}_{kl})(\mathbf{u}_{kl} \cdot \mathbf{u}_{ij}) - 3(\mathbf{u}_{ij} \cdot \mathbf{u}_{jk}) \\
& \times (\mathbf{u}_{jk} \cdot \mathbf{u}_{li})(\mathbf{u}_{li} \cdot \mathbf{u}_{ij}) - 3(\mathbf{u}_{ij} \cdot \mathbf{u}_{kl})(\mathbf{u}_{kl} \cdot \mathbf{u}_{li}) \\
& \times (\mathbf{u}_{li} \cdot \mathbf{u}_{ij}) - 3(\mathbf{u}_{jk} \cdot \mathbf{u}_{kl})(\mathbf{u}_{kl} \cdot \mathbf{u}_{li})(\mathbf{u}_{li} \cdot \mathbf{u}_{jk}) \\
& + 9(\mathbf{u}_{ij} \cdot \mathbf{u}_{jk})(\mathbf{u}_{jk} \cdot \mathbf{u}_{kl})(\mathbf{u}_{kl} \cdot \mathbf{u}_{li})(\mathbf{u}_{li} \cdot \mathbf{u}_{ij})], \quad (5)
\end{aligned}$$

$$D(ijkl) = D_3(r_{ij})D_3(r_{jk})D_3(r_{kl})D_3(r_{li}), \quad (6)$$

where Θ_i is the angle subtended by any triplet of atoms and \mathbf{u}_{ij} is the unit vector in the direction from atom i to atom j . The damping functions were taken in the form:

$$D_n(r_{ij}) = \begin{cases} \exp\left[-\mu_n\left(\beta_n \frac{r_o}{r_{ij}} - 1\right)^2\right] & r_{ij} \leq \beta_n r_o \\ 1 & r_{ij} > \beta_n r_o, \end{cases} \quad (7)$$

where μ_n and β_n are free parameters and r_o is the dimer equilibrium distance. The total number of free parameters to be fitted in the potential (1)–(7) is 21. In some cases, it is useful to include in the exchange potential, two exponential functions which can change sign of the exchange contribution for certain geometries.

For the two-body dispersion energy, the dipole-dipole (r^{-6}), dipole-quadrupole (r^{-8}), and dipole-octopole plus quadrupole-quadrupole (r^{-10}) interactions were taken into account. For the three-body dispersion energy the well-known Axilrod-Teller⁵⁵ expression was used, whereas for the four-body dispersion energy the expression derived by Bade⁵⁶ was incorporated. The angular part of the four-body dispersion energy contains many terms which have a strong tendency to cancel each other because of the nature of their angular dependence. So, in some cases it is sufficient to use only the exchange four-body term. The damping function $D_n(r_{ij})$ is added to all dispersion terms. The reason for this is described in Refs. 41,42.

Next, we describe the parameter optimization procedure using Ag_n clusters as an example. We found efficient to use two steps in the parameter optimization procedure. In the first step, we optimize the parameters of V_2 and V_3 in Eq. (1), separately, using for V_2 the calculated *ab initio* potential curve of Ag_2 and for V_3 the calculated *ab initio* potential surface of Ag_3 . The number of calculated NLSD points on the energy curve and surface was not less than 10 per fitting parameter of the V_2 and V_3 potentials. In the second step, we calculate the nonadditive energy of the cluster under study:

$$E_{\text{nonadd}}(\text{Ag}_n) = E_b(\text{Ag}_n) - V_2(\text{Ag}_n), \quad (8)$$

where $E_b(\text{Ag}_n)$ is the cluster binding energy, and fit the sum $V_3 + V_4$ to the nonadditive *ab initio* energy $E_{\text{nonadd}}(\text{Ag}_n)$. For V_3 , the parameters found at the first step are used as the initial set. In the fit of $V_3 + V_4$, for a better reproduction of the three-body energy, it is more effective to add to the $E_{\text{nonadd}}(\text{Ag}_n)$ the energy $E_3(\text{Ag}_3)$ of those triangles which are absent in the Ag_n cluster geometry. In order to provide a better accuracy, the number of NLSD calculated energies for

TABLE I. Values of the optimized parameters of the *ab initio* model potential for the Ag_6 cluster.

Parameter	Numerical values
A_2 (a.u.)	4.960
α (\AA^{-1})	0.989
C_6 (a.u. \AA^6)	123.473
C_8 (a.u. \AA^8)	9510.550
C_{10} (a.u. \AA^{10})	283616.427
μ_6	1.964
μ_8	0.589
μ_{10}	1.336
β_6	1.337
β_8	3.395
β_{10}	3.548
A_3 (a.u.)	2.067
γ_3 (\AA^{-1})	0.407
C_9 (a.u. \AA^9)	978.844
μ_3	3.164
β_3	1.597
A_4 (a.u.)	-0.949
γ_4 (\AA^{-1})	0.163
C_{12} (a.u. \AA^{12})	703050.339
μ_4	18.185
β_4	1.837

different Ag_6 structures was chosen not less than 5 per the number of parameters in the V_3 and V_4 potentials.

Once the analytic form of the model potential and the parameter optimization procedure are established, we try to match accurate quantum-mechanical electronic energies of a large variety of selected Ag_n structures. In the following, we will refer to the case of the Ag_6 cluster, although the procedure will be analogous for other clusters of different size. Because of the great number of calculations to be performed on dimers, trimers up to hexamers, we require not only a reliable, but also a flexible quantum-mechanical method appropriate for the study of these relatively heavy compounds. This is the reason why we resort to density functional theory as a tool to compute total electronic energies. In particular, we work inside the Kohn-Sham scheme and use the all-electron NLSM method which, in addition to local spin density terms, involves gradient corrections of both, the exchange and correlation functionals.^{47–49} All contributions are included in a self-consistent field process for higher accuracy. Calculations were performed with the use of the DGAUSS computational package.⁵⁷ An optimized procedure based on nonlinear least-squares method was also required to fit the parameters of the *ab initio* model potential. In Eq. (7), the theoretical value of the Ag_2 equilibrium distance, $r_o = 2.66 \text{\AA}$, was used.⁴⁸

Table I shows the numerical values of the 21 parameters for the Ag_6 potential. It is important to note that this set of parameters is valid only for the $n=6$ case. However, the procedure for constructing the *ab initio* model potential can be applied to clusters of arbitrary size using the *ab initio* data of the corresponding cluster. Therefore, our model potential is size-dependent in the sense that although its analytical expression is the same for any cluster size, the potential parameters depend on each specific size. This is justified since on the one hand it can not be expected that a single set of

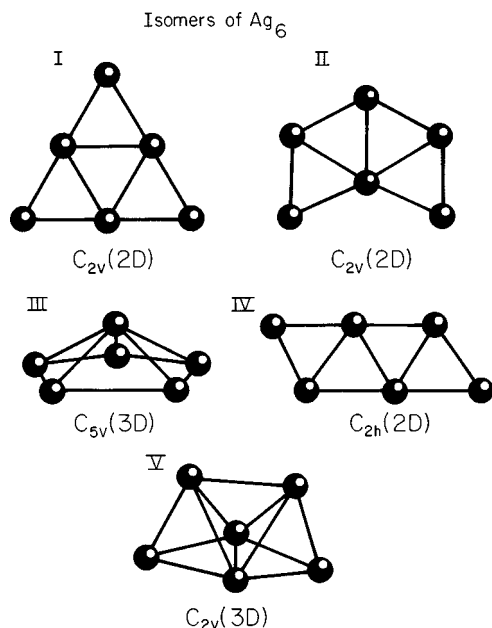


FIG. 1. Optimized geometries of the five most stable isomers of the Ag_6 cluster obtained using the *ab initio* many-body model potential.

parameters, defining the cluster potential energy surface, could describe correctly the complexity in the physical behavior of clusters of any size. On the other hand, it is not a realistic problem to find an analytical expression for the dependency of parameters on clusters size. The *ab initio* model potential obtained by the procedure described above also reproduces well the energetics of dimers and trimers, which is important for the study of cluster fragmentation.

III. MOLECULAR DYNAMICS SIMULATION, RESULTS AND DISCUSSION

We use the potential given in Eqs. (1)–(7) to calculate analytically its first derivatives with respect to the atomic Cartesian coordinates and generate the forces acting on each cluster atom. A constant-energy MD code was implemented with such forces to calculate structural and dynamical cluster properties. The Newton equations of motion were solved using the Verlet algorithm⁵⁸ with a time step of 1 fs, giving 0.05% of accuracy in the total energy conservation, even in runs as large as 10^6 time steps. Initial values of coordinates and momenta were chosen to yield a nontranslating and nonrotating cluster.

Several Ag_6 cluster isomers were obtained combining constant energy MD method and simulated annealing and quenching techniques.³⁰ These are the best currently available procedures to find global and local minima of potential energy surfaces (PES). They allow us to test the results by varying cooling rates and initial configurations. The structures obtained using such methods correspond to stable configurations associated to minima of the cluster multidimensional PES. In a typical calculation, we used a disordered cluster structure at a temperature, $T=2000$ K, as initial configuration, and performed MD simulations in which the total energy was decreased until the cluster structure no longer changed on further cooling ($T=10^{-4}$ K). Several initial conditions corresponding to different disordered cluster structures and cooling rates in the range of $10^{11}-10^{13}$ K s⁻¹ were used to obtain stable Ag_6 cluster isomers as minima of the PES.

Figure 1 shows the structures of the five most stable isomers obtained during the simulated annealing and quenching procedures. In Table II, the binding energy information for each cluster isomer is presented. As expected, the lowest-energy isomer corresponding to a two-dimensional trigonal C_{2v} structure obtained by following the above procedure, agrees with the results from *ab initio* NLSD calculations.⁴⁸ Isomers I, III, and V are well-known metal cluster structures used as prototypes of atomic configurations with $n=6$.⁴⁶⁻⁴⁸ On the other hand, isomers II and IV have only been seldom considered as stable metal cluster configurations. In this work, they are found as local minima of the PES. These two planar structures, according to the model potential calculations, are more stable than the three-dimensional isomers, III and V, respectively. The binding energy, E_b , for the MD-optimized structures corresponding to the five isomers was also calculated by the NLSD method. The last two columns of Table II show those values and the relative error with respect to the values obtained through the *ab initio* model potential. It is observed that the binding energy ordering, calculated using the NLSD method, does not coincide completely with the model potential calculation, which make the three-dimensional structures (isomers III and V) more stable than isomers II and IV, respectively. This fact reflects that the optimized structures obtained with the NLSD method and the simulated annealing and quenching MD procedures, do not necessarily coincide due to numerical errors remaining in the fitting of the parameter values. However, the relative error is small (except for the case of isomer IV), indicating that the parameter optimization is good enough. In

TABLE II. Structural information and binding energies of the five most stable structures of the Ag_6 cluster, calculated from the *ab initio* model potential (V) and by the NLSD method (E_b).

Isomer	Geometry	Symmetry (dimension)	$V(\text{eV/atom})$	$E_b(\text{eV/atom})^a$	$\left \frac{E_b - V}{E_b} \right $
I	trigonal	C_{2v} (2D)	-1.200	-1.205(-1.206)	0.004
II	incomplete hexagon	C_{2v} (2D)	-1.183	-1.142(-1.170)	0.036
III	pentagonal pyramid	C_{5v} (3D)	-1.172	-1.177(-1.180)	0.005
IV	triangular chain	C_{2h} (2D)	-1.170	-0.993(-0.994)	0.179
V	tripyramidal	C_{2v} (3D)	-1.069	-1.080(-1.109)	0.010

^aThe values in parentheses are obtained after an optimization of the cluster geometry by the NLSD method.

TABLE III. Many-body, exchange, and dispersion energy contributions to the binding energy of the Ag₆ cluster isomers in eV, calculated from the *ab initio* model potential.

Isomer	V	V_2	V_3	V_4	V_{exch}	V_{dis}
I	-7.202	-12.509	15.525	-10.218	82.155	-89.357
II	-7.099	-12.535	15.601	-10.165	82.464	-89.563
III	-7.030	-14.412	21.024	-13.641	93.422	-100.452
IV	-7.022	-12.604	14.929	-9.347	82.624	-89.646
V	-6.411	-16.809	27.086	-16.689	106.739	-113.150

fact, such errors are within the accuracy of first principles calculations like NLS. According to our calculations,⁴⁸ the preciseness of the NLS method for the silver dimer is about 5% for the equilibrium distance and 10% for the dissociation energy. One of the possible origins for the large errors in the model potential description of the isomer IV is due to the low weight of the high energy structures in the fitting procedure.

Thus, the model potential is a good approximation of the true PES for the low-lying isomers of Ag₆ and can be used to describe the temperature behavior of the clusters up to evaporation. The latter is also provided by the optimization procedure, in which model potentials for dimers and trimers are optimized together with the cluster model potential.

In Table III, we present a decomposition of the model potential V in its many-body, V_m , exchange, V_{exch} , and dispersion, V_{dis} , contributions for the five isomers, where we designate:

$$V_{\text{exch}} = \sum_{m=2}^4 V_{m,\text{exch}}, \quad (9)$$

$$V_{\text{dis}} = \sum_{m=2}^4 V_{m,\text{dis}} \quad (10)$$

Although the model potential V reproduces the NLS results with good accuracy, it contains fitted parameters, therefore it can not be expected that V_{exch} and V_{dis} reproduce the exact theoretical values of the exchange and dispersion energies.

However, the trend in the relative variation of their values for different isomers can be instructive. It is also evident that V_{dis} is not the pure dispersion energy because of the damping function corrections which take into account the influence of the exchange effect. According to the data of Table III, it follows that the three-body repulsive forces make the three-dimensional structures less stable than the planar isomers. This also was shown in the *ab initio* calculation of silver clusters.⁴⁹ On the other hand, considering the exchange and dispersion contributions it can be concluded that the large magnitude of the repulsive exchange forces, notwithstanding of the larger contributions from the dispersion terms, is the reason of less stability of three-dimensional with respect to two-dimensional structures.

Below, results on the thermal stability and dynamical behavior of the Ag₆ cluster are presented. The lowest-energy two-dimensional trigonal C_{2v} structure was first considered. A dynamical study of this isomer is interesting due to its isomerization into two- and three-dimensional structures.⁴¹ The cluster dynamical behavior is monitored by the short-time average (over 5 vibrational periods) of the kinetic energy (STAKE) as a function of time.⁵⁹ Thermal stability is studied by calculating the root-mean-square bond-length fluctuations given by

$$\delta = \frac{2}{n(n-1)} \sum_{i<j}^n \frac{[\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2]^{1/2}}{\langle r_{ij} \rangle}, \quad (11)$$

where r_{ij} is the distance between atoms i and j and $\langle \dots \rangle$ denotes time average.⁵⁹

Figure 2 shows the time dependence of STAKE for three values of the cluster total energy. At low total energies (lower curve), the cluster vibrates around its equilibrium configuration (C_{2v} structure), giving an almost constant value for this quantity (solidlike behavior). At intermediate total energies (middle curve), STAKE shows a multimodal distribution of values as a function of time indicating the coexistence of several Ag₆ cluster isomers, cf. Ref. 30. At this energy, the potential energy minima visited by the cluster corresponds to two-dimensional structures. We call this

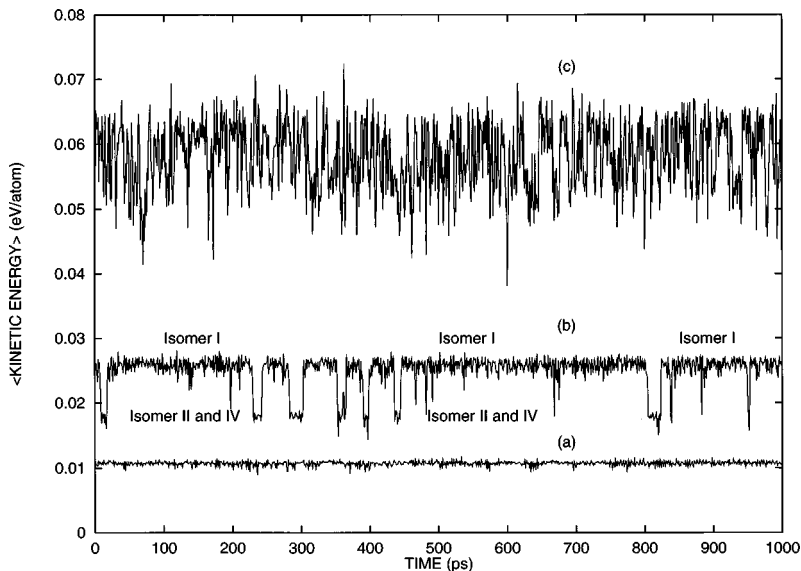


FIG. 2. Short-time average of the cluster kinetic energy as a function of time for three values of the Ag₆ total energy. Total energies (in eV/atom) corresponding to the three curves are: (a) -1.178; (b) -1.146; (c) -1.066. The trigonal two-dimensional C_{2v} structure was used as initial configuration in the MD simulation. Labels on curve (b) indicate the regions in which the corresponding isomers are obtained after the quenching procedures.

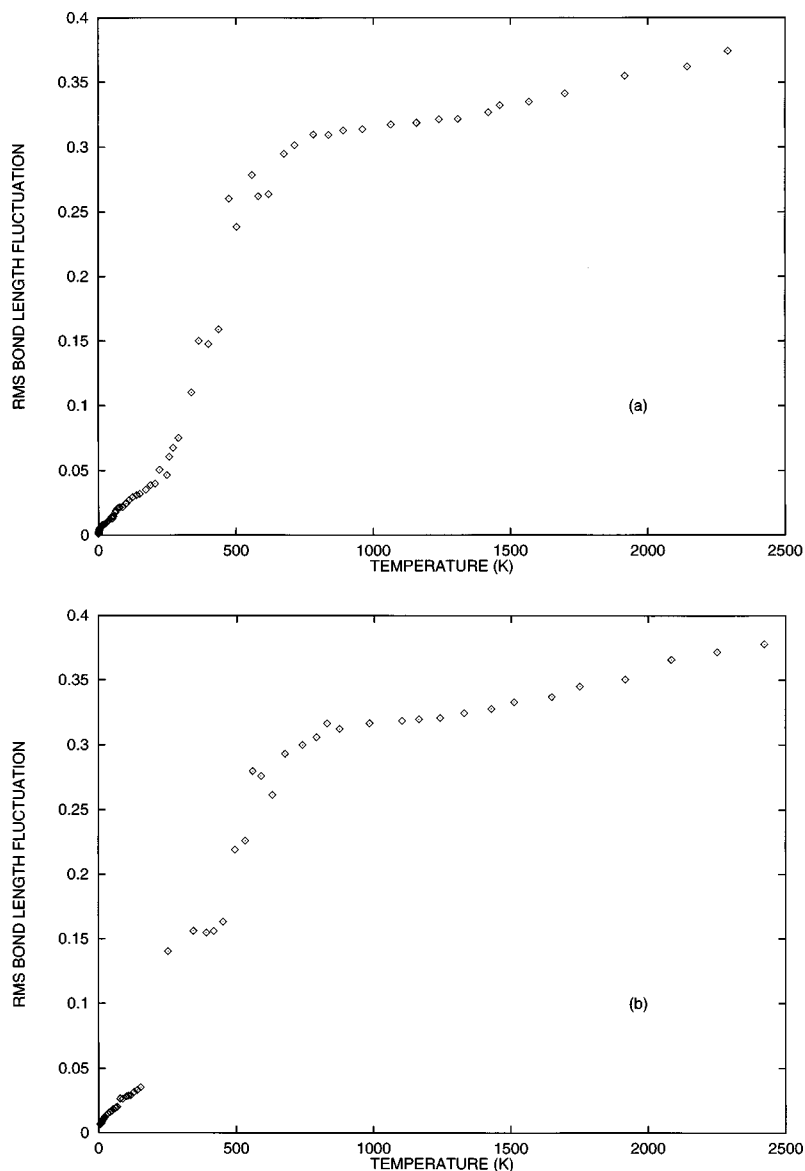


FIG. 3. Temperature dependence of the root-mean-square bond-length fluctuation of the Ag_6 cluster: (a) trigonal, C_{2v} , and (b) pentagonal pyramid, C_{5v} , structures.

behavior two-dimensional isomerization. The existence of these isomers is detected by direct visualization of the cluster configurations as a function of time, and by making quenching procedures using the cluster coordinates recorded at the points corresponding to values of low kinetic energy (high potential energy) shown in curve (b) of Fig. 2. The two-dimensional isomers which are more frequently seen, in addition to the C_{2v} structure are the incomplete hexagon with a central atom (isomer II) and an elongated structure of equilateral triangles, formed by two parallel linear chains of three atoms (isomer IV). At a higher total energy (upper curve), three-dimensional cluster isomers are also observed. The pentagonal pyramid (C_{5v}), the tripyramidal configuration (C_{2v}), and other less symmetric structures were observed during the visualization of the cluster trajectory at this energy. The STAKE now shows large fluctuations due to fast cluster structural changes. At this energy, the cluster dynamics becomes liquidlike.

The change in the root-mean-square bond-length fluctuations with the cluster temperature [$T=2\langle E_k \rangle / (3n-6)k$, where E_k is the total cluster kinetic energy and k is the

Boltzmann constant], is given in Fig. 3(a). It shows a two step meltinglike transition. At temperatures around 300 K, it presents an abrupt increase. This temperature corresponds to the case where the cluster total energy is in the range at which the isomerization phenomenon in the 2D [curve (b) of Fig. 2] was observed. At this temperature the cluster structure changes between several two-dimensional isomers described above. The second jump in δ [Eq. (11)], at 450 K, indicate the onset of liquidlike behavior (upper curve of Fig. 2).

The thermal stability as a function of the cluster temperature for the pentagonal pyramid configuration (isomer III) is of special interest.⁴² A dynamical study of this C_{5v} three-dimensional structure is motivated by the lack of symmetry existing in this configuration with respect to its pentagonal plane. The motion of the apex atom toward the plane, combined with the possibility of crossing the corresponding barrier, as was shown in our preliminary study,⁴² gives an interesting dynamical behavior. Figure 3(b) shows the temperature dependence of δ for this isomer. At low temperatures, it changes very slowly showing a linear behav-

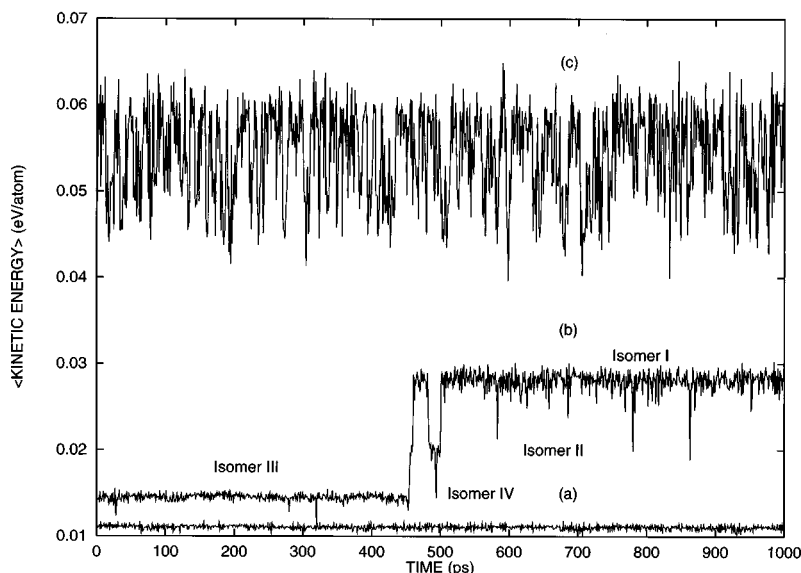


FIG. 4. Short-time average of the cluster kinetic energy as a function of time for three values of the Ag_6 total energy. Total energies (in eV/atom) corresponding to the three curves are: (a) -1.149 ; (b) -1.142 ; (c) -1.075 . The pentagonal pyramid C_{5v} structure was used as initial configuration in the MD simulation. Labels on curve (b) indicate the regions in which the corresponding isomers are obtained after the quenching procedures.

ior characteristic of the cluster thermal expansion through an increase in the amplitude of the atomic vibrational motion. At these temperatures the cluster behaves as a solidlike. In the temperature range of 300–500 K, the cluster departs from its vibrational motion around the pentagonal pyramid structure to display an isomerization behavior. At this stage, the main change is due to the displacement of the apex atom towards the pentagonal plane, following by the interchange between several two-dimensional structures, corresponding to local minima of the PES. Such isomerization phenomena results in a variation of the bond-length fluctuations from 10% to 20%. It is important to mention that three-dimensional isomers were not seen, within the simulation time, in this range of temperatures. The isomerization only occurs between two-dimensional structures.

Another important aspect of this dynamical behavior is that we did not observe, within the time scale of the simulation, that the apex atom returned to its original position or cross the pentagonal ring to the opposite side of the pentagonal pyramid. This effect is identified in Fig. 4 where the STAKE results are displayed for isomer III. At low total energies it shows an almost constant value indicating vibrational motion around the pentagonal pyramid configuration. However, at intermediate total energies the STAKE start at some value and remains around it by 450 ps. Later, this value increases indicating that structures with lower potential energy are being explored. As time increases, the STAKE values fluctuate around this higher kinetic energy and do not return to their original values corresponding to vibrations around the pentagonal pyramid structure. This behavior can be explained if we keep in mind that the Ag_6 cluster has several more stable planar and almost degenerate isomers. So, the probability for a return to a pyramidal structure is much lower than the isomerization between two-dimensional geometries. This situation is contrary to the NH_3 molecule case, where do not exist stable structures in the ground electronic state other than the pyramidal C_{3v} conformation.

Above 500 K, the Ag_6 cluster undergoes fast structural changes between 2D and 3D structures. Such behavior has

been related to a liquidlike phase, which extends beyond 2000 K. At about $T=2500$ K, the cluster fragmentation through dimer evaporation was observed. For comparison, in bulk Ag, the melting temperature is equal to 1235 K whereas the boiling point is around 2436 K.⁶⁰ Thus, our results indicate that the liquidlike behavior in the Ag_6 cluster begins at a lower temperature than in bulk, but the evaporation is observed almost at the same high temperature. Once the cluster dissociates at these high temperatures, the MD simulation was stopped.

The thermal behavior of the C_{2v} and C_{5v} Ag_6 isomers emerging from the above simulations shows similarities once the pentagonal pyramid configuration is lost at temperatures around $T=250$ K. In the temperature range of 300–500 K two-dimensional isomerization occurs in both calculations despite the availability of three-dimensional local minima with similar potential energy. Nevertheless, at higher temperatures, cluster fluctuations between two- and three-dimensional structures were observed for both isomers. At temperatures below 250 K, the thermal behavior of the C_{5v} isomer is different from that one corresponding to the C_{2v} structure because the MD simulation is exploring different basins of attraction. This effect is reflected through a different temperature dependence of the rms bond length fluctuation. Such isomeric-specific phenomenon was also seen in MD simulations of lithium clusters and is not related with any incomplete sampling of the phase space.^{18,20}

IV. SUMMARY AND CONCLUSIONS

A general approach to construct *ab initio* model potentials for metal clusters was applied to generate a potential for the Ag_6 cluster with further use in a MD simulation. Two new stable planar isomers with C_{2v} and C_{2h} symmetries were found as local minima of the cluster PES. Results on the thermal stability and dynamical behavior of this cluster were presented. Several structural changes as the cluster internal temperature increases were observed (solidlike, isomerization, liquidlike and fragmentation behavior) over a

broad range of temperatures. A two-dimensional isomerization phenomenon was observed at temperatures around 300 K, despite, the existence of three dimensional isomers with close energies. At higher temperatures fast fluctuations between two and three-dimensional cluster structures were observed.

The approach developed in our previous studies^{41,42} gives a systematic way to construct model potentials for atomic clusters. The analytical expressions of the different terms in the potential have a clear physical interpretation because they are based on the theory of intermolecular forces. Many-body nonadditive effects, particularly important in small metal clusters, are included not only through radial but also angular-dependent terms. The *ab initio* model potential for the Ag₆ cluster has the advantage that it is not adapted from bulk-related properties but arising from a finite-size (molecular) conceptions. Such an approach is necessary because bulk related potentials contain assumptions and parameters from the bulk phase which are not appropriate for finite systems, and their analytical expressions are not general enough to describe the richness of stable geometries existing in, for example, transition and noble metal clusters. However, the structural, dynamical, and thermal cluster properties predicted by this potential will depend on the accuracy of the *ab initio* data used to fit the parameter values and the number and weight of the different structures incorporated in the fitting procedure. In the present case, the NLSM method provides a reasonable microscopic description of the Ag₆ energetic properties. On the other hand, to find a model potential that describe simultaneously clusters, surfaces, and bulk properties is an unsolved problem in condensed matter physics. Along this direction, an analogous scheme have been recently proposed to study condensed matter systems in which *ab initio* forces of atomic configurations are used to fit the parameters of phenomenological potentials.⁶¹

Other advantages of the *ab initio* model potential used in this paper is that it contains explicit expressions for the interaction energy and its many-body decomposition through exchange and dispersion energies. We have the possibility of analyzing the dependence of all these physical quantities with respect to the atom-atom distances and cluster geometry which depend upon the electronic structure of the system under study. For example, the analysis of exchange and dispersion contributions to the model potential of different Ag₆ isomers reveals that it is the large magnitude of the repulsive exchange forces that leads to less stability of three-dimensional structures with respect to the two-dimensional ones. In sum, the advantages of the present approach are related to the reliability of the quantitative predictions obtained, due to the use of an accurate *ab initio* model potential, and the extended length of the MD simulation time, during which good statistics can be collected.

ACKNOWLEDGMENTS

This work was supported by the DGSCA-UNAM Supercomputer Center and by DGAPA-UNAM under Project No. IN101297. O.N. is a member of El Colegio Nacional.

- ¹The *Chemical Physics of Atomic and Molecular Clusters*, edited by G. Scoles (North-Holland, Amsterdam, 1990).
- ²*Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena, S. N. Khanna, and B. K. Rao (Kluwer Academic, Dordrecht, 1992), Vols. I and II.
- ³In *Proceedings of the Sixth International Symposium on Small Particles and Inorganic Clusters*, edited by R.S. Berry, J. Burdett, and A.W. Castleman, *Z. Phys. D* **26**, S26 (1993).
- ⁴*Clusters of Atoms and Molecules I*, Springer Series in Chemical Physics, edited by H. Haberland (Springer, Berlin, 1994), Vol. 52.
- ⁵V. Bonačić-Koutecký, P. Fantucci, and J. Koutecký, in Ref. 4, p.15, and references therein.
- ⁶R. S. Berry, in Ref. 4, p. 187, and references therein.
- ⁷J. Uppenbrink and D. J. Wales, *J. Chem. Soc., Faraday Trans.* **87**, 215 (1991), and references therein.
- ⁸H.-P. Cheng and U. Landman, *Science* **260**, 1304 (1993), and references therein.
- ⁹J. P. K. Doye, D. J. Wales, and R. S. Berry, *J. Chem. Phys.* **103**, 4234 (1995).
- ¹⁰W. Andreoni and G. Pastore, *Phys. Rev. B* **41**, 10243 (1990).
- ¹¹C. Rey, L. J. Gallego, J. García-Rodeja, J. A. Alonso, and M. P. Iñiguez, *Phys. Rev. B* **48**, 8253 (1993).
- ¹²R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ¹³R. Kawai and J. H. Weare, *Phys. Rev. Lett.* **65**, 80 (1990); U. Röthlisberger and W. Andreoni, *J. Chem. Phys.* **94**, 8129 (1991); J. Y. Yi, D. J. Oh, and J. Bernholc, *Phys. Rev. Lett.* **67**, 1594 (1991).
- ¹⁴C. Massobrio, A. Pasquarello, and R. Car, *Chem. Phys. Lett.* **238**, 215 (1995).
- ¹⁵P. Ballone, W. Andreoni, R. Car, and M. Parrinello, *Phys. Rev. Lett.* **60**, 271 (1988); U. Röthlisberger, W. Andreoni, and M. Parrinello *ibid.* **72**, 665 (1994).
- ¹⁶R. N. Barnett, U. Landman, A. Nitzan, and G. Rajagopal, *J. Chem. Phys.* **94**, 608 (1991).
- ¹⁷B. Hartke, D. A. Gibson, and E. A. Carter, *Chem. Phys. Lett.* **189**, 358 (1993).
- ¹⁸J. Jellinek, V. Bonačić-Koutecký, P. Fantucci, and M. Wiechert, *J. Chem. Phys.* **101**, 10092 (1994).
- ¹⁹P. Fantucci, V. Bonačić-Koutecký, J. Jellinek, M. Wiechert, R. J. Harrison, and M. F. Guest, *Chem. Phys. Lett.* **250**, 47 (1996).
- ²⁰V. Bonačić-Koutecký, J. Jellinek, M. Wiechert, and P. Fantucci, *J. Chem. Phys.* **107**, 6321 (1997).
- ²¹B. Hartke and E. A. Carter, *J. Chem. Phys.* **97**, 6569 (1992); D. A. Gibson, I. V. Ionova, and E. A. Carter, *Chem. Phys. Lett.* **240**, 261 (1995).
- ²²H. Popkie, M. Kistenmacher, and E. Clementi, *J. Chem. Phys.* **59**, 1325 (1973).
- ²³E. Clementi, F. Cavallone, and R. Scordamaglia, *J. Am. Chem. Soc.* **99**, 5531 (1977).
- ²⁴U. Niesar, G. Corongiu, E. Clementi, G. R. Kneller, and D. K. Bhattacharya, *J. Phys. Chem.* **94**, 7949 (1990).
- ²⁵E. Blaisten-Barojas and S. N. Khanna, *Phys. Rev. Lett.* **61**, 1477 (1988).
- ²⁶Z. X. Cai, B. D. Mahanti, A. Antonelli, S. N. Khanna, and P. Jena, *Phys. Rev. B* **46**, 7841 (1992).
- ²⁷C. E. Román-Velázquez and I. L. Garzón, *Z. Phys. D* **S26**, 134 (1993).
- ²⁸B. R. Cooper, J. Mei, and S. P. Lim, in *Stability of Materials*, NATO ASI Series B, edited by A. Gonis, P.E.A. Turchi, and J. Kudrnovský (Plenum Press, New York, 1996), Vol. 355, p. 443.
- ²⁹H. Diep, S. Sawada, and S. Sugano, *Phys. Rev. B* **39**, 9252 (1989); S. Sawada and S. Sugano, *Z. Phys. D* **20**, 259 (1991); **24**, 37 (1992).
- ³⁰J. Jellinek and I. L. Garzón, *Z. Phys. D* **20**, 239 (1991); I. L. Garzón and J. Jellinek, *ibid.* **20**, 235 (1991); in Ref. 2, Vol. I, p. 405; *Z. Phys. D* **26**, 316 (1993).
- ³¹F. Ercolessi, W. Andreoni, and E. Tossati, *Phys. Rev. Lett.* **66**, 911 (1991).
- ³²H.-P. Cheng and R. S. Berry, *Phys. Rev. A* **45**, 7969 (1992).
- ³³Z. B. Güvenç, J. Jellinek, and A. F. Voter, in Ref. 2, Vol. I, p. 411; Z. B. Güvenc and J. Jellinek, *Z. Phys. D* **26**, 304 (1993).
- ³⁴J. Uppenbrink and D. J. Wales, *J. Chem. Phys.* **98**, 5720 (1993).
- ³⁵J. García-Rodeja, C. Rey, L. J. Gallego, and J. A. Alonso, *Phys. Rev. B* **49**, 8495 (1994).
- ³⁶M. J. Lopez and J. Jellinek, *Phys. Rev. A* **50**, 1445 (1994).
- ³⁷S. K. Nayak, B. Reddy, B. K. Rao, S. N. Khanna, and P. Jena, *Chem. Phys. Lett.* **253**, 390 (1996).
- ³⁸A. Posada-Amarillas and I. L. Garzón, *Phys. Rev. B* **54**, 10362 (1996); I. L. Garzón and A. Posada-Amarillas, *ibid.* **54**, 11796 (1996).

- ³⁹N. N. Lathiotakis, A. N. Andriotis, M. Menon, and J. Connolly, *J. Chem. Phys.* **104**, 992 (1996).
- ⁴⁰O. B. Christensen, K. W. Jacobsen, J. K. Nørskov, and M. Manninen, *Phys. Rev. Lett.* **66**, 2219 (1991).
- ⁴¹I. L. Garzón, I. G. Kaplan, R. Santamaria, B. S. Vaisberg, and O. Novaro, *Z. Phys. D* **40**, 202 (1997).
- ⁴²I. G. Kaplan, I. L. Garzón, R. Santamaria, B. S. Vaisberg, and O. Novaro, *J. Mol. Struct.: THEOCHEM* **398-399**, 333 (1997).
- ⁴³T. Tani, *Phys. Today* **42**, 36 (1989).
- ⁴⁴T. Sun and K. Seff, *Chem. Rev.* **94**, 857 (1994).
- ⁴⁵D. W. Liao and K. Blasubramanian, *J. Chem. Phys.* **97**, 2548 (1992).
- ⁴⁶V. Bonačić-Koutecký, L. Češpiva, P. Fantucci, and J. Koutecký, *J. Chem. Phys.* **98**, 7981 (1993); V. Bonačić-Koutecký, L. Češpiva, P. Fantucci, J. Pittner, and J. Koutecký, *ibid.* **100**, 490 (1994).
- ⁴⁷I. G. Kaplan, R. Santamaria, and O. Novaro, *Int. J. Quantum Chem.* **S27**, 743 (1993).
- ⁴⁸R. Santamaria, I. G. Kaplan, and O. Novaro, *Chem. Phys. Lett.* **218**, 395 (1994).
- ⁴⁹I. G. Kaplan, R. Santamaria, and O. Novaro, *Mol. Phys.* **84**, 105 (1995); *Int. J. Quantum Chem.* **55**, 237 (1995).
- ⁵⁰I. G. Kaplan, *Theory of Intermolecular Interactions* (Elsevier, Amsterdam, 1986).
- ⁵¹W. Kolos, F. Nieves, and O. Novaro, *Chem. Phys. Lett.* **41**, 431 (1976).
- ⁵²O. Novaro and W. Kolos, *J. Chem. Phys.* **67**, 5066 (1977).
- ⁵³I. G. Kaplan, J. Hernández-Cobos, I. Ortega-Blake, and O. Novaro, *Phys. Rev. A* **53**, 2493 (1996).
- ⁵⁴L. Bruch and I. G. McGee, *J. Chem. Phys.* **59**, 409 (1973).
- ⁵⁵B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943).
- ⁵⁶W. L. Bade, *J. Chem. Phys.* **28**, 282 (1958).
- ⁵⁷J. Andzelm and E. Wimmer, *J. Chem. Phys.* **96**, 1280 (1992).
- ⁵⁸L. Verlet, *Phys. Rev.* **159**, 98 (1967).
- ⁵⁹J. Jellinek, T. L. Beck, and R. S. Berry, *J. Chem. Phys.* **84**, 2783 (1986).
- ⁶⁰*Handbook of Chemistry and Physics*, 72nd ed., edited by D. R. Lide (Chemical Rubber, Boca Raton, 1992).
- ⁶¹F. Ercolessi and J. B. Adams, *Europhys. Lett.* **26**, 583 (1994).