Global optimization method for cluster structures

Yin Wang,[1] Jun Zhuang,[2] and Xi-Jing Ning[1,*]
[1]*Applied Ion Beam Physics Laboratory, Institute of Modern Physics, Fudan University, Shanghai 200433, China*
[2]*Department of Optical Science and Engineering, Fudan University, Shanghai 200433, China*
(Received 31 March 2008; revised manuscript received 17 July 2008; published 25 August 2008)

A time-going-backward quasidynamics method is developed for global optimization of cluster structures, and its merits are examined by a simple classical mechanics model, indicating that the probability for the system to jump over high potential barriers by this method is much higher than that by common annealing methods. The method is then used to investigate the isomers of a Lennard-Jones cluster containing 38 atoms and the C_{60} cluster with the Brenner potential, and can easily give the most stable structures, which are difficult to obtain by common annealing methods. In addition, for small carbon clusters C_n $(n=21-30)$, most of the potential energies optimized by this method are much lower than those obtained by a genetic algorithm.

DOI: 10.1103/PhysRevE.78.026708 PACS number(s): 02.60.Pn, 02.70.Ns, 36.40.Mr

I. INTRODUCTION

The structures of clusters, especially the most stable ones, are a key to understanding the physical and chemical properties of clusters. However, the structural investigation of clusters is a challenge to scientists, both experimentally and theoretically. Even with modern probe techniques [1], for most clusters it is difficult to obtain unambiguous structural information from experiments. On the theoretical side, the potential energy surfaces (PESs) for clusters containing tens of atoms or more are usually related to very complex functions, and the search for their global minima has been proved to be an NP-hard problem [2]. Therefore, many global optimization methods have been developed to find the most stable isomers in recent decades [2–9]. A detailed discussion of the merits and flaws of various methods can be found in Ref. [10].

Global optimization methods based on annealing are widely used, and have proved successful in finding the global minima of many PESs. However, some global minima located in a potential well surrounded by high potential barriers usually cannot be reached by these methods unless the annealing starts from a specific "seed," which may be rather encountered occasionally in many attempts than forecast. For example, annealing methods, whatever strategies were adopted, can hardly find the global minimum of the Lennard-Jones (LJ) cluster containing 38 atoms (LJ_{38}) starting from a common seed [10–12]; the search for isomers of the C_{60} cluster with annealing methods lasted for a long time, but the most stable one was not found until 1998 [13]. These facts indicate that the ability of annealing methods on jumping over the high potential barriers may be limited.

In the present work, a quasidynamics method [14,15] based on a time-going-backward (TGB) model is developed for global optimization. The substantial differences between the time-going-backward quasidynamics method (TQM) and common annealing methods are examined carefully by quantitative analysis and numerical simulations. To check the effectiveness of our method, we use it to study the clusters of 38-atom LJ cluster and C_{60} with the Brenner potential function [16], and get the most stable isomers easily from arbitrarily selected seeds. In addition, for some small carbon clusters, it is shown that the potential energies of the structures obtained by TQM are lower than those found by an elaborately designed genetic algorithm [17].

II. TGB MODEL AND SEARCHING METHOD

A. Main idea of the TGB model

It is well known that, for a conservative system, the representative point density $D(p,q,t)$ in Γ space does not change along the phase trajectories according to the Liouville theorem, and the phase trajectories do not cross each other because the same mechanics system developing from the same initial condition has a unique motion rule. However, for a dissipative system, the motion of a particle is governed by the Langevin equation,

$$m\frac{d\nu}{dt} = \boldsymbol{F} - \alpha\nu + \boldsymbol{F}_R, \tag{1}$$

where $\boldsymbol{F}$, α, and $\boldsymbol{F}_R$ are the conservative force, a damping coefficient, and the random force, respectively. It can be deduced that, because of the damping force, the representative point density $D(p,q,t)$ increases with time, and representative points could ultimately converge at several points [18], such as the points $F1$ and $F2$ in Fig. 1(a), which can be

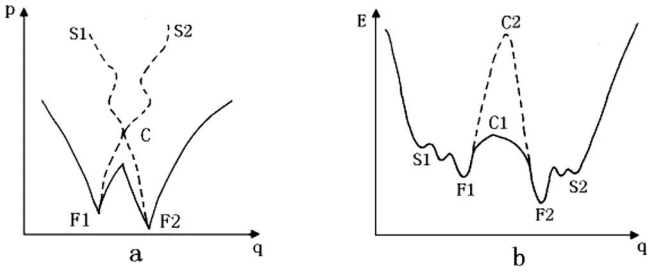

FIG. 1. Global optimization processes (a) in Γ space and (b) on a PES, on which the corresponding representative points are located.

*Corresponding author: xjning@fudan.edu.cn

treated as local minima of the system. If there is no random force, it is certain that the point $S1$ finally arrives at $F1$, and $S2$ arrives at $F2$. However, because of the random force, the phase trajectories can cross each other at some points, such as the cross point C in Fig. 1(a), and the initial points $S1$ and $S2$ may randomly arrive at final points $F1$ and $F2$. This is the underlying theory of some global optimization methods based on annealing.

The annealing processes shown in Γ space [Fig. 1(a)] can also be expressed on the PES as shown in Fig. 1(b), where the initial points $S1$, $S2$, the cross points $C1$, $C2$, and the final points $F1$, $F2$ are located. Supposing the annealing process starts from a random seed, e.g., $S1$, the global minimum $F2$ can be easily reached if the potential barrier between $F1$ and $F2$ is not high, as shown by the real line $(C1)$. Whereas, if the potential barrier between $F1$ and $F2$ is as high as the dashed line shows $(C2)$, the system may be trapped in $F1$ because it does not have enough kinetic energy to jump over the barrier, causing the global minimum $F2$ being missed. One way to solve this problem is to replace the seed by, for example, the unpredictable one $S2$, and another is to heat the system above $C2$ by resetting the velocities of the atoms with Maxwell distribution at high temperatures. The heating may be abrupt or multistepped. For the former all the atoms are simultaneously assigned velocities at higher temperatures, while for the latter partial atoms are warmed up gradually by randomly resetting bigger velocities. In the followed cooling process, the system may return to $S1$, or jump over $C2$ to $F2$. However, the probability to reach $F2$ is very low, which will be shown by a simple model in the following, leaving the trapping problem unsolved.

In the present work, we use another heating method [14,15] to ameliorate the trapping problem. For a classical mechanics system initially located at $F1$, we integrate Eq. (1) with a negative time step, i.e., compel the system to "evolve" from its "present" to its "past," which is named the TGB procedure in this paper. This seems a trivial trick, but can result in a profound effect on the dissipative system, because the damping force $-\alpha v(t)$ in Eq. (1) no longer dissipates energy, but contributes kinetic energy to the system. Clearly, if the average intensities of the random forces remain unchanged, i.e., the random forces just lead to fluctuation of the kinetic energy, the system is heated by the damping force. Unlike the heating by velocity rescaling, the heating by the damping force can keep the moving directions of the atoms unchanged on the whole; these are mainly determined by the directions of the initial velocities. As a result, the probability for a system to jump over a high barrier should be as high as that over a low barrier, because the directions of the initial velocities are isotropic. This phenomenon can be tested by the simple model shown in Fig. 2. Initially, 10 000 atoms are placed on the base of a potential well with its left barrier kept at 1 eV and its right barrier modulated between 1 and 10 eV in a series of simulations. Then the atoms are assigned velocities taken from a Maxwell distribution at a temperature T, corresponding to 1 eV. In the followed evolution, the interactions between the atoms are ignored, the damping coefficient α and the random force $\boldsymbol{F}_R$ are taken with the same magnitudes as the parameters of our calculations in Sec. III. It should be pointed out that in this system the time goes either in the normal way or in the TGB way, leading to very different results. After the system evolves for enough time, the probabilities for the atoms to escape from the potential well are counted and listed in Table I. When the time goes in the normal way, the probabilities for jumping over high barriers are very low, though all the atoms finally escape from the potential well because of the effects of random forces. However, for the TGB procedure, the probabilities for escaping from the high barrier are as high as those from the low barrier. Clearly, the probability for the system to jump over a high barrier in the TGB way is much higher than that obtained by common methods. If the atoms are assigned velocities at much higher temperatures, for example corresponding to 100 eV, the two barriers may be jumped over with similar probabilities in normal way, but for the cluster optimization process, such abrupt temperature change may lead to the explosion of clusters.

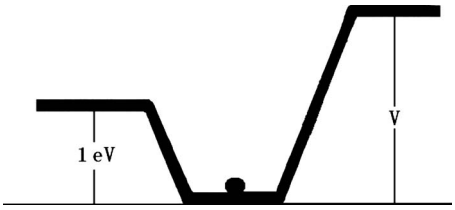

FIG. 2. 10 000 atoms at the base of a potential well with its left barrier kept at 1 eV and right barrier changed between 1 and 10 eV.

B. Simulation model and details

The common cluster growth in the gas phase can be divided into three steps: production of isolated atoms from a solid source at high temperatures, condensation to form crude clusters in the course of cooling and evolution at a low temperature to form the final products. Based on these steps,

TABLE I. The probabilities for atoms to escape from the potential well.

Right barrier (eV)	Normal dissipative system (%)		TGB dissipative system (%)	
	Left	Right	Left	Right
1	50.62	49.38	49.87	50.13
2	74.05	25.95	51.35	48.65
5	98.15	1.85	52.28	47.72
10	99.97	0.03	52.05	47.95

some annealing methods cool a seed from high temperatures with different cooling strategies to search for the global minimum. A quasidynamics method, which is also a kind of annealing method, was developed to search for the isomer spectra of small carbon clusters by Sheng *et al.* [19]. Isolated atoms, which are assigned an initial temperature much higher than the melting point of their bulk materials, are placed in a cubic box, on which periodic boundary conditions are applied. The system is cooled toward a lower temperature T, at which the configuration of the cluster hardly changes, by resetting the velocity of one randomly selected atom every interval Δt with the equation

$$v^{\text{new}} = (1-\theta)^{1/2} v^{\text{old}} + \theta^{1/2} v^{\text{T}}(\xi), \tag{2}$$

where θ is a parameter between 0 and 1, and $v^T(\xi)$ is a velocity selected randomly from the Maxwell velocity at T via a random number ξ. Velocity resetting with Eq. (2) corresponds to taking the damping coefficient $\alpha = m\theta/2\Delta t$ and the random force $F_R = m\theta^{1/2} v^{\text{T}}(\xi)/\Delta t$ in Eq. (1), where m is the atomic mass [20]. According to our previous work [19], 0.1 is an appropriate value for θ and a small change of it does not affect the searching results much. The interval Δt is determined by the method described in detail in Ref. [19]. After the system is in equilibrium at T, it is then further cooled to 0 K by the damping method [21] to obtain an isomer and the corresponding potential energy. This simple method is successful in obtaining the global minima of some small carbon clusters [19,22], and the global minimum may be found among dozens of simulation results, but for clusters larger than 30 atoms enormous computing time has to be spent to find the global minima.

Instead of starting from isolated atoms, here we start searching from an arbitrarily selected seed at a lower temperature T_i, and the seed evolves in the TGB way. That is, the integral time step is negative, and the velocity of one randomly selected atom is rescaled at every interval Δt using Eq. (2) in the inverse form as $v^{\text{new}} = [v^{\text{old}} - \theta^{1/2} v^{\text{T}}(\xi)]/(1-\theta)^{1/2}$ (backward). When the temperature of the system reaches a higher temperature T_f, which is usually near to but lower than the melting point of the bulk materials, the system is then cooled by the quasidynamics method (forward). The above backward-forward cycle is always allowed to run several times from the same seed to obtain a group of results. If the lowest energy obtained in the group is lower than the energy of the seed, the corresponding isomer will be treated as a new seed for further simulations. If no lower-energy isomer can be found after enough cycles, the simulations are finished, and the last seed is deemed to be the global minimum. Generally, according to our experience, 50 cycles is enough for most clusters.

III. RESULTS AND DISCUSSIONS

A. LJ 38-atom cluster

LJ clusters are good examples for evaluating the efficiency of a global optimization method [10]. For LJ_{38}, the lowest-energy isomer is a face-centered-cubic (fcc) truncated octahedron, rather than based on an icosahedral structure like many other LJ clusters, and it is much harder to find its global minimum by common annealing methods because of its complex PES [12]. In the following, to compare the search abilities of different annealing methods, the TQM and several annealing methods are used to search for the most stable isomer of LJ_{38}. Taking the parameters of argon for the LJ potential [23], we first perform the search by the quasidynamics method. Briefly, 38 isolated atoms evolve from 80 K in a cubic box with periodic boundary conditions applied, during which Eq. (2) is used to cool the system every 7000 fs. After the system reaches 10 K, it is then cooled to 0 K by the damping method [21], and the structure and corresponding potential energy are recorded. This procedure runs 80 times, and the lowest-energy isomer of the 80 results is shown in Fig. 3(a). It is easy to understand that the fcc truncated octahedron LJ_{38} isomer [Fig. 3(b)] is not obtained, because there existed some high potential barriers between the seed [Fig. 3(a)] and the global minimum [Fig. 3(b)] [12], and these barriers cannot be jumped over easily by many annealing methods. Taking the isomer shown in Fig. 3(a) as a seed, then we performed the search by the TQM. The interval Δt for using Eq. (2) or its inverse form on the system is still 7000 fs, while T_i and T_f are 10 and 40 K, respectively. We do 160 simulations from this seed, and the global minimum with the fcc truncated octahedron structure shown in Fig. 3(b) is obtained 11 times.

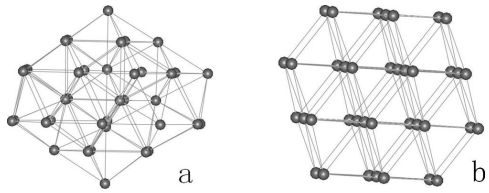

FIG. 3. The (a) seed and (b) global minimum structures of the LJ_{38} cluster.

In order to test the efficiency of the TGB procedure further, next we perform the annealing simulations in two different ways from the same seed [Fig. 3(a)]. In the first way, the system is assigned a high temperature T_f directly, and then evolves as in the quasidynamics method. These simulations are also performed 160 times, but no global minimum is obtained. One may think that the evolution time in this process is much shorter than that in the TGB procedure, so that the probability for finding the global minimum in the annealing process is reduced. Accordingly, in the second annealing method, the system is gradually heated from T_i to T_f by resetting the velocity of one randomly selected atom every interval Δt with Eq. (2), which takes nearly the same time as the heating by the TGB procedure, and then the system evolves as in the quasidynamics method. Among the 160 simulations, only one reaches the global minimum. Clearly, the TGB procedure can greatly increase the likelihood of isomers to jump over the potential barriers, as analyzed in Sec. II A.

In recent years, some new methods, for example the parallel tempering method [24], have been developed to improve the traditional annealing methods to cope with high barriers. In the parallel tempering scheme, several simula-

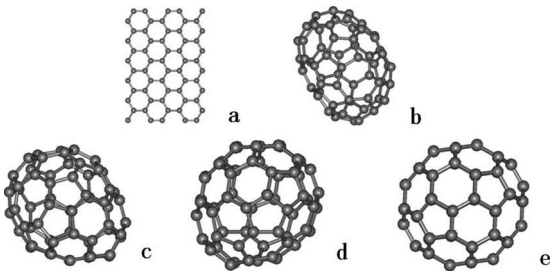

FIG. 4. Structures of the seed during the optimization process by the TQM.

tions from different seeds are performed simultaneously at different total energies, during which two simulations at different energies attempt to exchange their configurations with some predetermined probabilities. The action of the exchange equates to heating or cooling the system abruptly, which is similar to the heating in the general annealing process. In this sense, the efficiency of the parallel tempering method to cause jumping over high barriers may be improved if the system is heated in the TGB way.

B. C_{60} cluster

The C_{60} cluster is also used to test the search efficiency of our TGB method. The Brenner potential function is still adopted to describe the interaction of the carbon atoms [16,25]. For the parameters of Eq. (2), the interval Δt is 450 fs, and T_i and T_f are 1000 and 4000 K, respectively. We first perform 16 simulations with the TQM starting from a graphite layer with 60 atoms named $S1$ [Fig. 4(a)], whose potential energy per atom (PEPA) is −6.723 37 eV. Among the 16 results, the lowest energy is −7.000 78 eV, which corresponds to the structure shown in Fig. 4(b), named $S2$. Taking $S2$ as a new seed, we obtain $S3$ shown in Fig. 4(c) in the next 16 results, then $S3$ to $S4$ [Fig. 4(d)] and $S4$ to $S5$ [Fig. 4(e)] with the same procedure. The lowest energies obtained in every group, i.e., the energies of the seeds for the following group, are illustrated in Fig. 5. That is, in every 16 simulation groups, a new seed with energy lower than that of the previous one can always appear, and the perfect C_{60} ($S5$) with a PEPA of −7.045 16 eV is found in the fourth group. A similar procedure has been successfully used for producing the most stable isomer of C_{36} [15]. These results indicate that

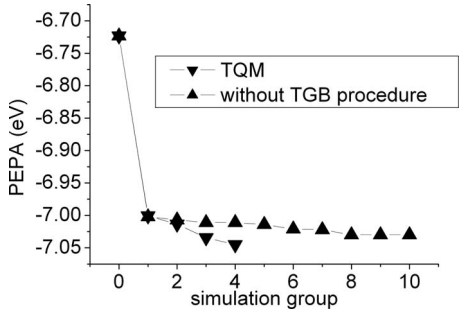

FIG. 5. PEPA of the seeds obtained in every group during the optimization processes by the TQM and the general annealing method without the TGB procedure.

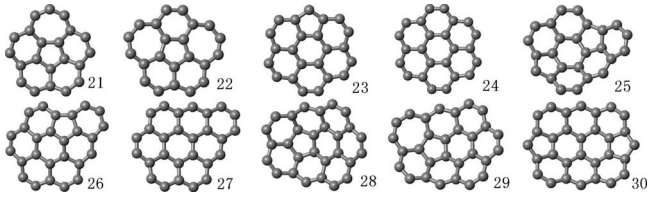

FIG. 6. TQM-optimized structures of C_{21}–C_{30} at T_f=3000 K.

our TQM is a robust approach for searching for the lowest-energy structure.

By comparison, the system is assigned a high temperature T_f directly, and annealed by resetting the velocity of one randomly selected atom with Eq. (2) every 450 fs. Once the lowest energy obtained in a group of 16 results is lower than the energy of the seed, the corresponding isomer is treated as a new seed for the followed simulations. The lowest energies of every group are illustrated in Fig. 5. Unfortunately, after ten groups of simulations, the energy of the most optimized isomer is still very high.

Historically, people tried to obtain the most stable C_{60} by different annealing methods with the Tersoff potential [26], tight-binding method [27–30], and Car-Parrinello method [31], but it was in 1998 that the most stable C_{60} was first obtained from a common seed by the Brenner potential after about 200 ns annealing [13]. In our searching process, a backward-forward cycle needs about 1 ns, which is two orders of magnitude smaller than the annealing time in Ref. [13].

C. C_n (n=21–30) clusters

In addition to annealing methods, the genetic algorithm (GA) is another very popular global optimization method, and a comparison of the TQM with GAs is very interesting. We optimize C_n (n=21–30) clusters with the Brenner potential, and compare our results with the results in Ref. [17] obtained by a GA. For the parameters of Eq. (2), the intervals Δt for different clusters are determined by the method described in Ref. [19], and T_i and T_f are 1000 and 3000 K, respectively. It is noted that T_f=3000 K is now as high as the temperature in the third growth step of carbon clusters mentioned in Sec. II B [13]. The searching procedure is the same

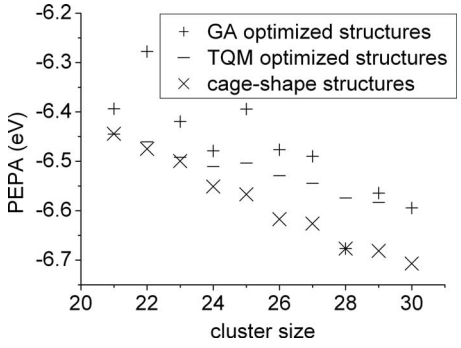

FIG. 7. PEPA of the isomers obtained by different optimization processes.

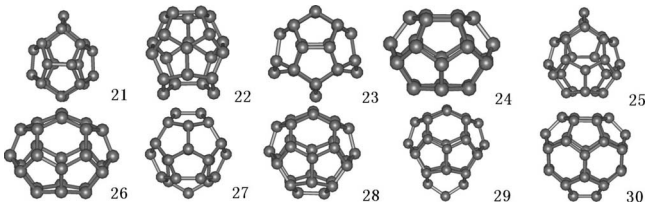

FIG. 8. Cage-shaped structures of $C_{21}-C_{30}$. These can be obtained by the TQM from a high-energy cage-shaped seed.

as that for C_{60}. The simulations also start from graphite layers with given number of atoms, and if the lowest energy obtained in a group of 16 results is lower than the energy of the seed, the corresponding isomer is treated as a new seed for further simulations. The TQM-optimized structures shown in Fig. 6 are obtained in the fifth group. The potential energies of these structures and the GA-optimized structures [17] are shown in Fig. 7. For $C_{21}-C_{27}$ and C_{29}, the potential energies obtained by the TQM are lower than those from the GA; for C_{30}, the two methods have the same result. For C_{28}, however, the lowest-energy structure obtained by the TQM is a flat-shaped isomer, whose energy is higher than that of the cage-shaped isomer (Fig. 8) given by the GA method. Obviously, most of the results obtained by the TQM are consistently lower than those by the GA, with the single exception of C_{28}. Of course, the GA is not a standard algorithm, but can work with very different design choices or control parameters. So it can be expected for a deliberately designed GA to find these global minima of small carbon clusters. However, it is not very easy to design a correct GA. Notably, the TQM is a simple method with only a few parameters that need to be adjusted, and the "simply designed" TQM sometimes outperforms an "elaborately designed" GA.

Considering that the cage-shaped C_{28} found by the GA is not found in the fifth group by our method we then did more TQM simulations with T_f increased to 4000 K, and successfully obtained cage-shaped C_{25} and C_{28} (Fig. 8) finally. Furthermore, if the simulations start from cage-shaped structures with higher energies, the TQM can quickly produce all the cage-shaped C_n ($n=21-30$) clusters (global minima) (Fig. 8), whether $T_f=3000$ or 4000 K. The potential energies of these structures are also illustrated in Fig. 7.

The above simulations indicate that the TQM-optimized results are not completely independent of the seeds. This problem can be partially solved by a predetermined seed procedure as used in Sec. III C for the LJ_{38} cluster, where a given number of atoms at higher temperatures are quenched to 0 K, producing various seed isomers. Using this procedure for small carbon clusters, we obtained cage-shaped seeds of $C_{25}-C_{30}$, from which the global minima can be found quickly. However, cage-shaped seeds of $C_{21}-C_{24}$ are not produced in our limited simulations by the predetermined seed procedure, for these cage seeds may reside in a very small part of the PES, and are very difficult to find even with many methods based on annealing. In the GA community, some recipes have been invented to solve this problem, and these recipes can be introduced to enhance the search ability of the TQM in the future.

IV. CONCLUSIONS

A global optimization method, named the time-going-backward quasidynamics method is developed in this paper. This method is conveniently realized by just setting a negative integral time step in the dynamics process. This trivial trick can notably help the system to jump over higher potential barriers during the optimization process, because when evolving in this way the damping force accelerates the atoms in the directions of their initial velocities and compels the atoms to climb up the barriers. In the structural optimization process, it means that the effectiveness of our TQM is high. As examples, the TQM is used for LJ_{38} and C_{60} clusters, and get the lowest-energy structures more easily than common annealing methods. For small carbon clusters, the potential energies of the structures obtained by the TQM are obviously lower than those by an elaborately designed genetic algorithm. This simple method can be used alone for many optimization problems, or the TGB idea can be introduced into many other annealing methods to improve their search abilities.

ACKNOWLEDGMENTS

This work is supported by the National Nature Science Foundation of China under Grant No. 10574030. Some of the calculations were performed on NHPCC of Fudan University and the Shanghai Supercomputing Center. We are grateful to J. H. Dai, W. Wei, and S. Y. Zhou for their help on some calculations of the small carbon clusters.

[1] S. J. L. Billinge and I. Levin, Science **316**, 561 (2007).
[2] S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, Science **220**, 671 (1983).
[3] N. Metropolis, A. W. Rosenbluth, N. N. Rosenbluth, and A. H. Teller, J. Chem. Phys. **21**, 1087 (1953).
[4] D. M. Deaven and K. M. Ho, Phys. Rev. Lett. **75**, 288 (1995).
[5] D. J. Wales and H. A. Scheraga, Science **285**, 1368 (1999).
[6] D. L. Freeman and J. D. Doll, J. Chem. Phys. **82**, 462 (1985).
[7] J. Lee J, H. A. Scheraga, and S. Rackovsky, J. Comput. Chem. **18**, 1122 (1997).
[8] T. Zhou, W. J. Bai, L. J. Cheng, and B. H. Wang, Phys. Rev. E **72**, 016702 (2005).
[9] W. S. Cai and X. G. Shao, J. Comput. Chem. **23**, 427 (2002).
[10] D. J. Wales and J. P. K. Doye, J. Phys. Chem. A **101**, 5111 (1997).
[11] D. J. Wales, M. A. Miller, and T. R. Walsh, Nature (London) **394**, 758 (1998).
[12] J. P. K. Doye and D. J. Wales, Z. Phys. D: At., Mol. Clusters **40**, 194 (1997).
[13] S. Maruyama and Y. Yamaguchi, Chem. Phys. Lett. **286**, 343

(1998).
[14] S. Y. Zhou, Y. Wang, and X. J. Ning, Acta Phys. Sin. **57**, 387 (2008).
[15] J. Gao, Z. Z. Lin, and X. J. Ning, J. Chem. Phys. **126**, 174309 (2007).
[16] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).
[17] C. Zhang, X. Xu, H. Wu, and Q. Zhang, Chem. Phys. Lett. **364**, 213 (2002).
[18] X. J. Ning and Q. Z. Qin, J. Chem. Phys. **110**, 4920 (1999).
[19] Y. Sheng, P. Li, and X. J. Ning, Chin. Phys. Lett. **21**, 2012 (2004).
[20] M. E. Riley, M. E. Coltrin, and D. J. Diestler, J. Chem. Phys. **88**, 5934 (1988).
[21] L. M. Raff, J. Chem. Phys. **95**, 8901 (1991).
[22] Y. Sheng, X. J. Ning, and P. Li, J. Chem. Phys. **121**, 2013 (2004).
[23] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
[24] H. Liu and K. D. Jordan, J. Phys. Chem. A **109**, 5203 (2005).
[25] T. Halicioglu, Chem. Phys. Lett. **179**, 159 (1991).
[26] P. Ballone and P. Milani, Phys. Rev. B **42**, 3201 (1990).
[27] J. R. Chelikowsky, Phys. Rev. Lett. **67**, 2970 (1991).
[28] J. R. Chelikowsky, Phys. Rev. B **45**, 12062 (1992).
[29] X. D. Jing and J. R. Chelikowsky, Phys. Rev. B **46**, 5028 (1992).
[30] C. Z. Wang, C. H. Xu, C. T. Chan, and K. M. Ho, J. Phys. Chem. **96**, 3563 (1992).
[31] J. Y. Yi and J. Bernholc, Phys. Rev. B **48**, 5724 (1993).