Front. Phys. China (2006) 3: 351—356
DOI 10.1007/s11467-006-0034-8

RESEARCH ARTICLE

**WU Zhi-min,WANG Xin-qiang, XIAO Xu-yang,
HE Huan-dian, LUO Qiang**

Thermodynamic properties of noble metal clusters: molecular dynamics simulation

Abstract The thermodynamics properties of noble metal clusters Au_N, Ag_N, Cu_N, and Pt_N (N =80, 106, 140, 180, 216, 256, 312, 360, 408, 500, 628, 736, and 864) are simulated by micro-canonical molecular dynamics simulation technique. The potential energy and heat capacities change with temperature are obtained. The results reveal that the phase transition temperature of big noble metal clusters ($N \geq 312$ for Au, 180 for Ag and Cu, and 360 for Pt) increases linearly with the atom number slowly and approaches gently to bulk crystals. This phenomenon indicates that clusters are intermediate between single atoms and molecules and bulk crystals. But for the small noble clusters, the phase transition temperature changes irregularly with the atom number due to surface effect. All noble metal clusters have negative heat capacity around the solid-liquid phase transition temperature, and hysteresis in the melting/freezing circle is derived in noble metal clusters.

Keywords noble metal cluster, thermodynamics properties, molecular dynamics

PACS numbers 61.46.-w, 68.65.+g, 71.15.Mb

WU Zhi-min,WANG Xin-qiang (✉), XIAO Xu-yang, HE Huan-dian, LUO Qiang
Department of Physics, College of Science, Chongqing University,
Chongqing 400044, China
E-mail: xqwang@cqu.edu.cn

WU Zhi-min
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Science,
Beijing 100080, China

Received July 5, 2006

1 Introduction

Nanoclusters, or nanoparticles, containing tens to thousands of atoms or molecules, play important roles in science and technology. Clusters are intermediate between single atoms and molecules and bulk materials. They are the building blocks of nano-science. Their properties are often peculiar, being qualitatively different from those of their constituent parts (either atoms or molecules) and from those of macroscopic pieces of materials [1]. In particular, nanoclusters can present properties that vary dramatically with size. This opens the possibility of controlling these properties by controlling precisely their formation process.

Applications of clusters in innovative technology seem to be endless, as they range from industrial catalysis to the miniaturization of electronic devices. For example, gold nanoparticles studded with shot segments DNA [2] could form the basis of an easy-to-read test to single out genetic sequences [3]. It has also been discovered that the Renaissance masters in Umbria, Italy, used nanoparticles in the decoration of majolicas with lustre [4, 5]. Lustre consists of a thin film containing silver and copper clusters with diameters up to a few tens of nanometers, often of noncrystalline structure. Due to the inclusion of these nano-particles, luster gives beautiful iridescent reflections of different colors.

However, one difficulty is that by most experimental techniques it is practically impossible to prepare a large ensemble of nanoclusters with narrow size distribution. Furthermore, even for a given cluster size, a distribution of structural isomers occurs. Therefore, the interpretation of experimental data is very complicated [6] and thus computer simulations are considered not only as complementary but also essential components of cluster studies. Using empirical potential models, molecular dynamics (MD) [7—12] simulation is an ideal tool for investigating the physics of such clusters.

The nature of phase transition in finite systems is a subject of considerable interest in the context of the interrelationship between thermodynamic, energetic and dynamic size effects in clusters. Several groups have been devoted to the phase transition of noble metal clusters. The melting behavior of noble metals (Au$_N$, Ag$_N$, Cu$_N$, and Pt$_N$, N = 2–23) has been studied by Garcia-Rodeja *et al.* using MD simulations [13]. The results show that all the 13-atom clusters have high melting temperature, and that a pre-melting phenomenon occurs in the 14-atom and 20-atom cluster. Gold clusters have been studied by Cleveland *et al.* [14, 15], Lee *et al.* [16], and Li *et al.* [17]. All these studies agree that a solid-solid structural transition from the low temperature optimal structures to icosahedral structures takes place below the melting temperature. Baletto *et al.* have studied the freezing of silver liquid nano-droplets by MD simulations with realistic cooling rates r_c in the range 0.1–5 K/ns [18]. They found that it is not possible to avoid the formation of a large percentage of small icosahedra if freezing takes place after the growth is completed. MD simulations on melting of free copper clusters (55-, 147-, and 309-atoms) were studied by Vakealahti *et al.* [19]. They suggested that the dynamics coexistence (DC) process could extend to medium-size metal clusters. Platinum cluster containing 55 atoms has been studied by Baletto [20]. The simulations show that it has entropic effects and kinetic trapping.

However, comparing with the extensive studies and abundant results of sodium cluster [21—25], a lot of properties, especially the thermodynamic properties around the phase transition temperature of noble metal clusters are still obscure. Furthermore, there is no systemic study of the free noble metal clusters between 50—1000 atoms. Motivated by these reasons, in this paper, the melting and freezing processes of Au$_N$, Ag$_N$, Cu$_N$, and Pt$_N$ (N = 80, 106, 140, 180, 216, 256, 312, 360, 408, 500, 628, 736, and 864) clusters are calculated with MD technique and embedded-atom model (EAM) [26, 27] in details. Their thermodynamics properties are analyzed and some fascinate results are shown.

2 Computational methods and details

A key point in the theoretical study of clusters is the choice of an appropriate energetic model. In any case, the use of semi-empirical potentials is in practice a necessary tool for the study of medium or large size clusters. Here, the EAM model is used, which is an many-body potential proven to reproduce various static and dynamic properties of transition and noble metals, in either bulk or finite configurations. The model is "semi-empirical" in the sense that it approaches the total-energy from a local-electron-density viewpoint, but use a functional with parameters obtained from experiment (equilibrium, lattice constant, bulk modulus, elastic constants, etc.) [28]. Equations used by EAM are as follows:

$$E_{\text{tot}} = \sum_i F_i\left(\rho_{h,i}\right) + \frac{1}{2}\sum_i \sum_{j(\neq i)} \phi_{ij}\left(R_{ij}\right) \tag{1}$$

$$\rho_{h,i} = \sum_{j(\neq i)} \rho_j^{\alpha}\left(R_{ij}\right) \tag{2}$$

where, E_{tot} is total energy, $\rho_{h,i}$ is the host electron density at atom i due to the remaing atoms of the system, $F_i(\rho)$ the energy to embed atom i into the background electron density ρ, and $\phi_{ij}(R_{ij})$ is the core-core pair repulsion between atoms i and j separated by the distance R_{ij}. In this paper, the electron density and two-body potential are taken as reference [27]:

$$f(r) = f_e\left(\frac{r_{1e}}{r}\right)^{\beta} \tag{3}$$

$$\phi(r) = \phi_e\left(\frac{r_{1e}}{r}\right)^{\gamma} \tag{4}$$

where

$$f_e = \frac{E_{\text{C}}}{S_{\beta}\Omega}, \quad S_{\beta} = \sum_{i=1}^{n}\frac{N_i}{k_i^{\beta}} \tag{5}$$

$$\phi_e = 2\frac{E_{\text{C}}}{S_{\gamma}}, \quad S_{\gamma} = \sum_{i=1}^{n}\frac{N_i}{k_i^{\gamma}} \tag{6}$$

where E_{C} is crystal binding energy, Ω is the atomic volume, the sum is over n neighbor shells, N_i is the number of atoms of the ith shell, and K_i is the ratio of the radius of the ith shell to the nearest-neighbor distance. All these parameters are taken from reference [29].

The initial spherical noble metal clusters are obtained from a bulk crystal with face-centered-cubic (FCC) structure by cutting off the atoms outside the sphere of a given radius R, Then, the clusters are annealed, which means to heat the clusters from room temperature (300 K) up to the temperature near the melting point, and subsequently cooling them down to the room temperature slowly. After that, the obtained clusters are taken as initial structures to start the simulations.

During simulation processes, we change the total energy (or temperature) of a cluster by rescaling a random-velocity from Maxwell distribution for a given temperature to each atom. Because Maxwell distribution is a statistical distribution, the supposed initial temperature and the statistical temperature after relaxation may be different greatly. So it is very difficult to control the temperature precisely. To reduce computational cost, the time steps of thermalization are decided by the changing of the total energy (increase or decrease in last simulation). The most important is to have enough simulation time to ensure that the system reach its equilibrium after each thermalization. Because the bigger fluctuation in the smaller clusters cannot avoid, the more simulation time is needed to solve this problem at present. In our calculations, each simulation time steps exceeds 4×10^6 with 2fs each step. Around the melting and freezing points, to get the clusters' equilibrium state, more simulation time (more than 4×10^7 steps) is used than other positions.

In addition, it is also worth noting that the present study does not aim to quantitative prediction of the physical and chemical behavior of copper clusters, but rather to the qualitative exploration of the thermodynamic properties in connection with the occurrence of melting and freezing processes.

3 Results and discussion

The most common method for studying the phase transition is the calculation of the caloric, that is, the potential energy of the clusters as a function of T [22]:

$$U = U(T) \tag{7}$$

during phase transition, $U(T)$ will show a sharp jump, corresponding to a peak in the heat capacity curve $c(T)$:

$$c(T) = \partial U(T) / \partial T \tag{8}$$

the melting/freezing points of the clusters are defined as the temperature corresponding to the extremum of the heat capacity [30].

The calculated caloric for the Au_{312}, Ag_{312}, Cu_{408}, and Pt_{360} clusters during melting and freezing processes are shown as examples in Fig. 1. (The curves for other clusters are qualitatively similar.) Sharp jumps indicate solid / liquid phase transition. It can be seen that the phase transition occurs in a range of temperature, meaning that the melting begins at the surface of the cluster and generally goes into the core until the whole clusters is totally melt and *vice versa*. In Fig. 2, sharp drops of the heat capacities at the melting and freezing temperature, derived from the differentiation of the caloric data, are displayed.

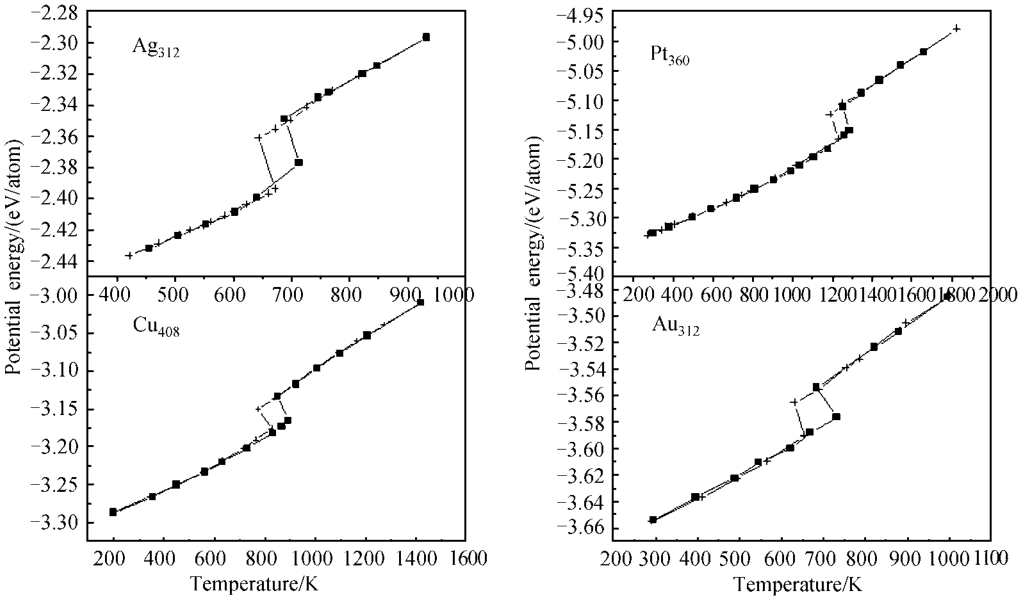

Fig. 1 The caloric curves for Au_{312}, Ag_{312}, Cu_{408}, and Pt_{360} clusters during melting (*solid squares*) and freezing (*pluses*) processes.

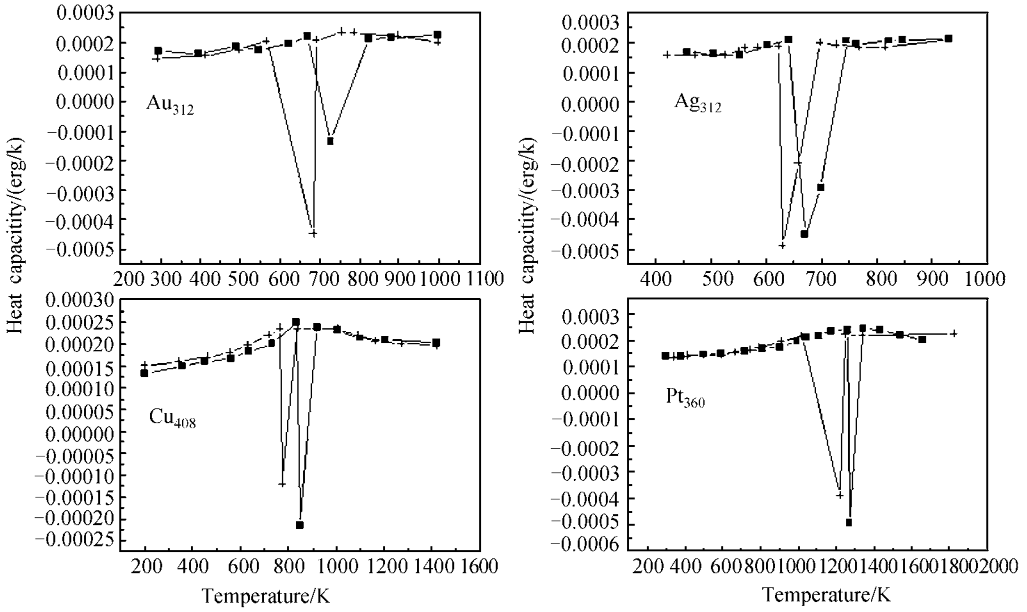

Fig. 2 Heat capacities vs temperature during melting (*solid squares*) and freezing (*crosses*) process for Au_{312}, Ag_{312}, Cu_{408}, and Pt_{360} clusters.

3.1 Melting and freezing temperature

The melting and freezing temperature of Au_N, Ag_N, Cu_N, and Pt_N clusters with different sizes are summarized in Table 1 and plotted in Fig. 3. One can find firstly the melting and freezing temperature are all lower than their bulk crystal (1337 K for gold, 1235 K for silver, 1356 K for copper, and 2045 K for platinum), which is consistent with previous works [30—32], while Shavartsburg and Jarrold even found that tin cluster ions containing 10—30 atoms have melting temperature at least 50 K above the bulk one [33]. Secondly, the melting/freezing temperature changes with cluster size diversely, some increase monotonously with the cluster size (platinum clusters, and freezing temperature of copper cluster), but others change irregularly with their size for small cluster (gold cluster, silver cluster and melting temperature of copper cluster). It should be noted that some previous studies have shown the phase transition temperature should be proportional to the cube root of the clusters' atom number [31], while others argue irregular behaviors of the melting point of cluster [29, 34].

3.1.1 Gold clusters

From Fig. 3, one can find that the melting and freezing temperature increasing sharply with cluster size for gold cluster smaller than 200 atoms，it reaches a peak around 180 K rapidly, then it has a small decrease. The phase transition temperature increases quickly again for gold cluster between 216 and 312 atoms. Finally, it increases linearly with the atom number of big gold cluster slowly.

3.1.2 Silver clusters

The phase transition temperature of silver cluster changes similarly with gold cluster. Firstly, it increases sharply with cluster size, reaches a local maximum around 140 atoms, then it goes through a quickly decrease smaller than 180 atoms. Finally, it increases linearly with the atom number of big silver cluster.

3.1.3 Copper clusters

Comparing with gold and silver clusters, the phase transition temperature of copper clusters changes more simply. For small copper clusters, the melting temperature has a local maximum around 140 atoms, then, it increases linearly with the atom number for cluster bigger than 180 atoms. However, it is more interesting that the freezing temperature increases linearly with the atom number for all the copper clusters.

3.1.4 Platinum clusters

The phase transition temperature of platinum cluster is most simply. It increases with the atom number monotonously. However, the curves of phase transition temperature can be plotted as two parts. One is that the cluster size is smaller than 312 atoms, the phase transition temperature increase linearly with the atom number sharply, another is that the cluster size is bigger than 360 atoms, it also increase linearly with the atom number, but much slowly.

To sum up, the phase transition temperature of big noble cluster ($N \geq 312$ for Au, 180 for Ag and Cu, and 360 for Pt) increase linearly with the atom number slowly and approaches gently to bulk crystals. This phenomenon indicates that clusters are intermediate between single atoms and molecules and bulk crystals. But for the small noble metal clusters, the phase transition temperature changes irregularly with the atom number due to surface effect. It is needed to point out that the phase transition temperature of platinum cluster increase monotonously with the atom number, but the curves have two slopes, sharp for the small cluster and slow for the big cluster.

Table 1 Melting and freezing temperature of various noble metal clusters, with N atom number of cluster, T_m melting temperature, T_f freezing temperature, and ΔT the difference of T_m and T_f.

N	Au			Ag			Cu			Pt		
	T_m/K	T_f/K	ΔT/K	T_m/K	T_f/K	ΔT/K	T_m/K	T_f/K	ΔT/K	T_m/K	T_f/K	ΔT/K
80	537	501	36	528	496	32	703	657	46	948	904	44
106	573	528	45	582	541	41	726	668	58	997	958	39
140	609	562	47	723	632	91	769	679	90	1 069	1 021	48
180	654	598	56	640	601	39	752	694	58	1 130	1 066	64
216	638	593	45	649	611	38	769	711	58	1 179	1 125	54
256	687	648	39	661	621	40	782	728	54	1 233	1 173	60
312	727	683	44	671	630	41	802	743	59	1 263	1 213	50
360	739	697	42	681	641	40	827	761	66	1 272	1 224	48
408	748	706	42	687	647	40	848	775	73	1 297	1 255	42
500	767	725	42	703	663	40	883	819	64	1 309	1 268	41
628	786	744	42	724	683	41	916	847	69	1 314	1 273	41
736	807	767	40	743	701	42	950	888	62	1 329	1 283	46
864	829	783	46	764	724	40	986	921	65	1 342	1 298	44

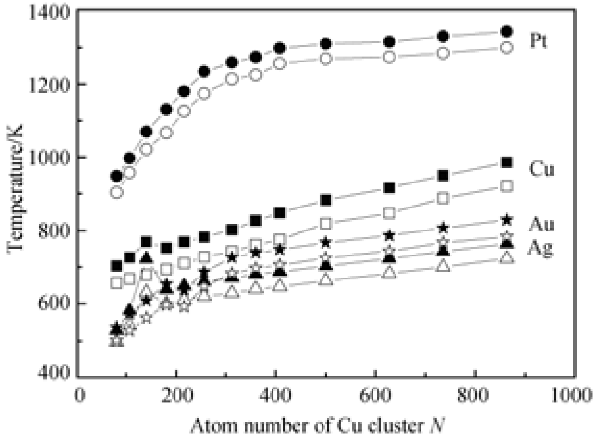

Fig. 3 Melting (*solid symbols*) and freezing (*open symbols*) temperature vs atom number of gold (*pentagons*), silver (*triangles*), copper (*squares*), and platinum (*circles*) clusters.

3.2 Negative heat capacity

In our calculations, all the curves of potential energy vs temperature (in Fig. 1) have knee points around solid-liquid phase transition temperature. Around these points, as the energy increases(or decreases), the temperature decreases(or increases) inversely. Figure 2 shows that each curve of heat capacity vs temperature has a negative peak, their heat capacities are negative around phase transition temperature.

It is well accepted that a system will become warmer if one adds energy to it. However, negative heat capacities have been well known in astrophysics [35, 36], where energy can be added to a star cluster when cools down. A similar effect has been calculated for melting atomic clusters [37, 38]. In fact, the negative micro-canonical heat capacity in Na_{147} was reported experimentally by Martin Schmidt *et al*. near its solid-liquid transition temperature [39]. More recently, negative heat capacities have also been found theoretically for Na_N ($N = 135$, 142, and 147) clusters around their melting-like transition by micro-canonical MD simulations [40].

Martin Schmidt *et al.* [39] consider nanocluster as a small micro-canonical system, to avoid partly molten states, the system prefers to convert some of its kinetic energy into potential energy instead and the cluster probably become colder while its total energy increases. To understand the micro-mechanism of negative heat capacity in our clusters and test Martin Schmidt's view, the atom distribution in the clusters have been studied. As an example, Fig. 4 is the radial distribution of atoms in the Au_{312} cluster before and after melting. Obvious peaks in Fig. 4 (a) represent the shell structure (order state) of solid state of the cluster. As the radius increase, the peaks become sharper due to the atoms of the shell increase from inner to outer. However, the corresponding peaks in Fig. 4 (b) become lower and wider, some even has disappeared, representing the disordered structure of liquid state. This abrupt change of the cluster structure at the solid/liquid transition will lead to the potential energy jump suddenly (increase or decrease acutely). Because the increase (or decrease in freezing processes) of the total energy can't compensates the decrease (or increase in freezing processes) of the potential energy, the kinetic and potential energy translate into each other, leads to a lower (in melting processes) or higher (in freezing processes) temperature. The negative heat capacity occurs in the clusters.

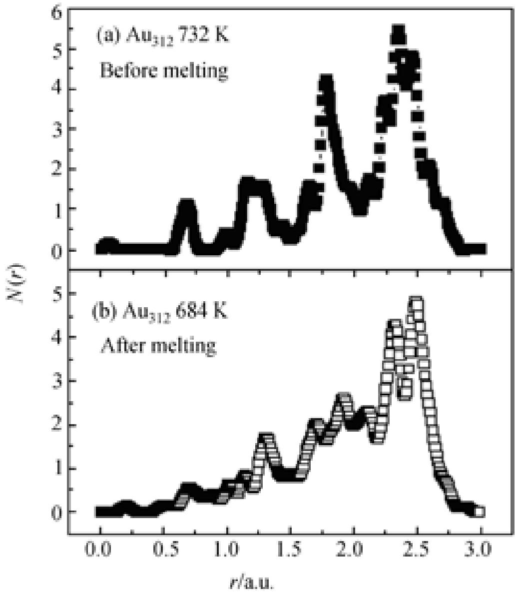

Fig. 4 The radial distributions of atoms in the Au_{312} cluster: (**a**) Before melting, (**b**) After melting.

3.3 Hysteresis effect

As well known, the melting point and freezing point are at the same temperature for the bulk crystal, but for cluster, the situation is not so. Hesteresis is observed in melting/freezing circle (Fig. 1). The freezing points are about a few decade Kevins lower than the melting points for the same cluster (Fig. 3 and Table 1). Hysteresis effect indicates that transforming from order (solid phase) to disorder (liquid phase) is easier than disorder to order, obeying the principle of entropy increase for the micro-canonical ensemble. It also indicates that the melting temperature is probably much closer to the bulk thermodynamic transition temperature than the freezing temperature. To the best of our knowledge, hysteresis effect in the melting/freezing circle is reported in noble metal cluster system for the first time, while it has been expected theoretically [41] and observed experimentally in the case of lead cluster system [42].

4 Conclusions

The thermodynamics properties around phase transition temperature of Au_N, $Ag_{N,}$ Cu_N, and Pt_N (N = 80, 106, 140, 180, 216, 256, 312, 360, 408, 500, 628, 736, and 864) clusters have been calculated by micro-canonical MD technique carefully. The results show that the phase transition temperature of big noble cluster ($N \geq 312$ for Au, 180 for Ag and Cu, and 360 for Pt) increase linearly with the atom number slowly and approaches gently to bulk crystals'. This phenomenon indicates that clusters are intermediate between single atoms and molecules and bulk crystals. But for the small noble clusters, the phase transition temperature changes irregularly with the atom number due to surface effect. All the nanoclusters have negative heat capacities around phase transition temperature. It could be attributed to the potential energy jump by the abrupt change of cluster structure. Hysteresis effects are concluded in all the noble metal clusters.

References

1. Yaroslav G.. C. and Lawrence S. B., J. Phys. Chem. B, 2001, 105: 11605
2. Alivisatos A. P., Johnsson K. P., Peng X. G., et al., Nature (London), 1996, 382: 609
3. Alivisatos A. P., Sci. Am. (Int. Ed.), 2001, 285: 66
4. Borgia I., Brunetti B., Mariani I., et al., Appl. Surf. Sci., 2002, 185: 206
5. Padeletti G. and Fermo P., Appl. Phys. A: Mater. Sci. Process, 2003, 76: 515
6. Chushak Y. G. and Bartell L. S., J. Phys. Chem. B, 2001, 105: 11605
7. Ercolessi F., Andreoni W., and Tosatti E., Phys .Rev. Lett., 1996, 193: 355
8. Chen X. S., Zhao J. J., and Sun Q., Phys. Status Solid, 1996, 193: 355
9. Jellinek J., Beck T., and Berry R. S., J. Chem. Phys., 1986, 84: 2783
10. Lynden-Bell R. M. and Wales D. J., J .Chem. Phys., 1994, 101: 1460
11. Labastie P. and Whetten R. L., Phys. Rev. Lett., 1990, 65: 1567
12. Garzon I. L., and Jellinek J., Z. Phys., 1991, 20: 235
13. Garzon I. L. and Gallego L. J., Phys. Rev. B, 1997, 56: 6466
14. Cleveland C. L., Luedtke W. D., and Landman U. L., Phys. Rev. Lett., 1998, 81: 2036
15. Cleveland C. L., Luedtke W. D., and Landman U. L., Phys. Rev. B, 1999, 60: 5065
16. Lee Y. J., Nieminen R. M., Lee E. K., et al., Comput. Phys. Commun., 2001, 142: 201
17. Li T. X., Lee S. M., Han S. J., et al., Phys. Lett., 2002, 300: 86
18. Balleto F., Motttet C., and Ferrando R., Chem. Phys. Lett., 2002, 354: 82
19. Valkealahti M. and Manninen M., J. Phys.: Condens. Matter, 1997, 9: 4041
20. Balleto F., Mottet C., and Ferrando R., Phys. Rev. Lett., 2003, 90: 35504
21. Martin T. P., Naher U., Schaber H., et al., J. Chem. Phys., 1994, 100: 2322
22. Schmidt M., Kusche R., Kronmuller W., et al., Nature (London), 1998, 393: 238
23. Liu H. B., Perez R., Canizal G., et al., Sufr. Sci., 2002, 518: 14
24. Calvo F. and Spiegelman F., J. Chem. Phys., 2004, 120: 9684
25. Calvo F. and Spiegelman F., J. Chem. Phys., 2000, 112: 2888
26. Johnson R. A., Phys. Rev. B, 1988, 37: 3924
27. Johnson R. A., Phys. Rev. B, 1990, 41: 9717
28. Lewis L. J., Jensen P., and Barrat J. L., Phys. Rev. B, 1997, 56: 2248
29. Johnson R. A., Phys. Rev. B, 1989, 39: 12554
30. Wang L., Zhang Y. N., Bian X. F., et al. , Phys. Lett. A, 2003, 310: 197
31. Pawlow J., Surf. Sci, 1981, 106: 1
32. Martin T. P., Naher U., Schaber H., et al., J. Chem. Phys., 1993, 100: 2322
33. Shvartsburg A. A. and Jarrold M. F., Phys. Rev. Lett., 2000, 85: 2530
34. Frantz D. D., J. Chem. Phys., 2001, 115: 6136
35. Thirring W., Z. Phys., 1970, 89: 183403
36. Lynden-Bell D., Physica A, 1999, 87: 203401
37. Bixon M. and Jortner J., J. Chem. Phys., 1989, 91: 1631
38. Labastie P. and Whetten R. L., Phys. Rev. Lett., 1990, 65: 1567
39. Schmidt M., Kusche R., Hippler T., et al, Phys. Rev. Lett., 2001, 86: 1191
40. Reyes-Nava J. A., Garzon I. L., and Michaelian K., Phys. Rev. B, 2003, 67: 165401
41. Reiss H., Mirabel P., and Whetten R. L., J. Phys. Chem., 1988, 92: 7241
42. Kofman R., Cheyssac P., Aouaj A., et al., Surf. Sci., 1994 303: 231