

## Kinetics of nonequilibrium shape change in gold clusters

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The properties of gold clusters  $\text{Au}_N$  with  $N$  from 40 to 800 have been studied using constant temperature molecular-dynamics simulations and an empirical potential. A solid-liquid transition is clearly identified for this size range. For clusters of size  $N > 150$  it is also seen that surface atoms of a cluster start to diffuse well below the melting point. We also study the kinetics of shape change from an initial nonequilibrium elongated state to a final, close to equilibrium, compact shape. It is found that the radius of gyration  $r_g$  that reflects the cluster shape decays by different mechanisms depending on the temperature and cluster size. At most temperatures large solid clusters coalesce smoothly by surface diffusion, while smaller solid clusters maintain their nonequilibrium shape for a long time and then coalesce abruptly.

### I. INTRODUCTION

The solid-liquid transition of small clusters has been intensively investigated using molecular-dynamics (MD) and Monte Carlo simulation techniques. The early simulations were mostly performed using the Lennard-Jones potential,<sup>1</sup> and so are applicable to noble gas clusters. Recently, the focus of interest has shifted to metals as several many-body potentials have been developed to describe, in particular, fcc metals.<sup>2-4</sup> A number of theoretical studies of metal clusters concentrate on the equilibrium properties, such as the caloric curves (i.e., the relationship between internal energy and temperature), the mean-square displacements, and bond-length fluctuations, to identify the solid-liquid phase transition and other equilibrium properties.<sup>5-8</sup>

Our interest in this work is to study mass transport in small metal clusters. Two key issues we address are (1) the size and temperature range in which surface diffusion becomes an important mode of mass transport and (2) the rate at which highly nonequilibrium cluster shapes relax toward their close-to-equilibrium structure. These issues are important in understanding the growth morphology of thin metal films on solid surfaces, where many cluster coalescence events occur prior to the formation of a continuous thin film, and in understanding the thermal stability of nonequilibrium cluster shapes and quantum dots.

We used constant temperature MD and the Verlet algorithm. The caloric curves and the surface and bulk diffusion constants are calculated as a function of temperature. In the studies of nonequilibrium shape change, the initial structures are perfect fcc clusters, and we follow the evolution of the radius of gyration of the clusters  $r_g$  as a function of time, at constant temperature.

This paper is arranged as follows. Section II contains both a brief statement of the MD method and the results. Section III contains a summary and our conclusions.

### II. METHOD AND RESULTS

To study the equilibrium behavior of gold clusters, we performed simulations on clusters of  $N = 55, 177, 381,$

and 725 gold atoms which generally form a close-packed fcc structure in vacuum (the  $N = 55$  gold cluster is icosahedral). The empirical potential<sup>4</sup> we used is given by

$$V = -\frac{1}{2} V_0 \sum_{i=1}^N \left[ \left( \sum_{j \neq i} \exp[-2q(r_{ij} - 1)] \right)^{1/2} - A \sum_{j \neq i} \exp[-p(r_{ij} - 1)] \right],$$

where the parameters for gold are  $p = 10.15$ ,  $q = 4.13$ ,  $V_0 = 3.81$  eV, and  $A = 0.118$ . The four clusters we study approximately correspond to cluster radii of 2, 3, 4, and 5 lattice constants, respectively. Starting with the low-temperature crystal structure, we gradually heat up the clusters by increasing the velocity of each atom. The time step is taken to be  $4.24 \times 10^{-15}$  s, which is sufficient to ensure a temperature stable to 1%. We measured the internal energy averaged over 10 000 steps after equilibrating the clusters, typically for over 50 000 steps (equilibration was indicated by a stable internal energy). In Fig. 1(a), the caloric curves for the four clusters are presented. The arrows point to the transition points, which, as expected, increase as the cluster size increases. Figure 1(b) gives the specific heat for the same clusters. For all of the clusters studied, there is a clear indication of a liquid-solid transition, and the temperature of the transition increases with cluster size roughly as  $T_c(R) \sim T_c(\infty)(1 - R_c/R)$ , where  $R$  is the cluster radius. Smaller clusters probably need to be treated with more sophisticated potentials, and in some cases are known to deviate from the simple law stated above. Our data are broadly consistent with the experimental data<sup>9</sup> for gold clusters in the size range studied, although the melting temperatures are consistently higher than that found in experiment, and in calculations using the glue potential.<sup>9</sup>

The diffusion of atoms in the clusters was studied in a similar manner to the caloric curves. At sufficiently low temperatures the atoms in a solid phase are confined to have oscillatory motion near their equilibrium positions and the amplitudes of motion are small compared with

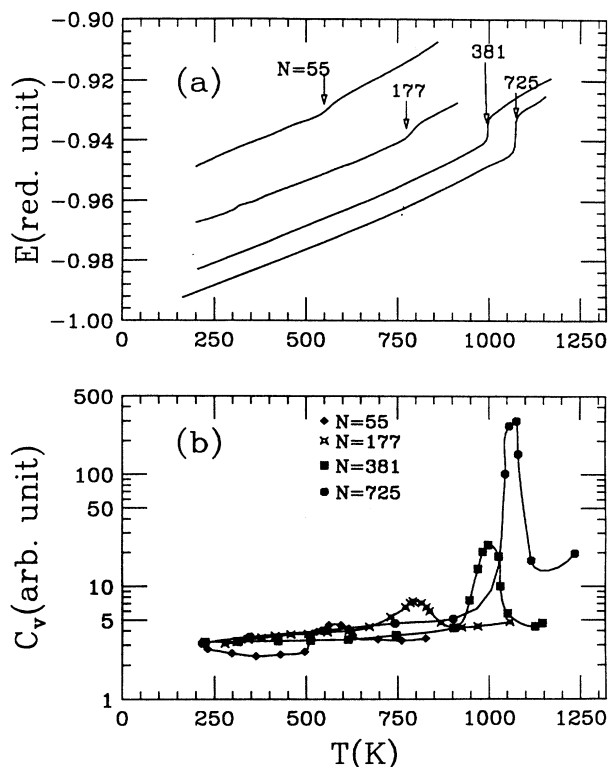


FIG. 1. Thermodynamic behavior of gold clusters. (a) The internal energy as a function of temperature and (b) the specific heat.

atomic separations, at least on the time scale of our simulations. In a liquid, atoms diffuse around in the cluster. However, even below the melting temperature of the clusters, surface atoms are active on large clusters. To illustrate this fact, we focus our attention on the  $N=725$  cluster first. We first present data in which we have averaged the mean-square displacement over all atoms in the

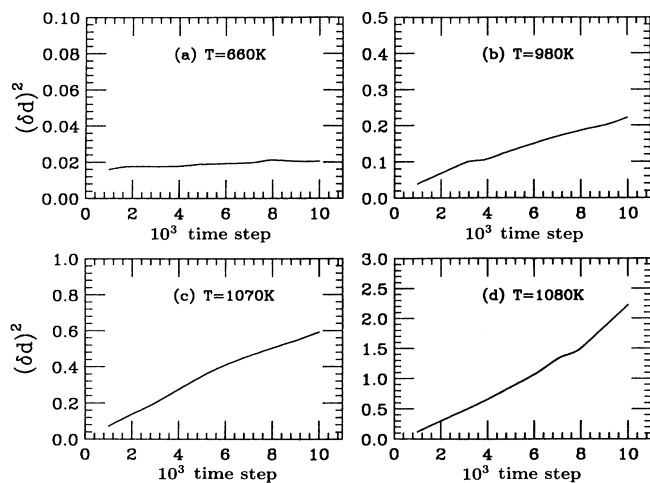


FIG. 2. The average mean-square displacement as a function of time for atoms in a  $N=725$  cluster for various temperatures.

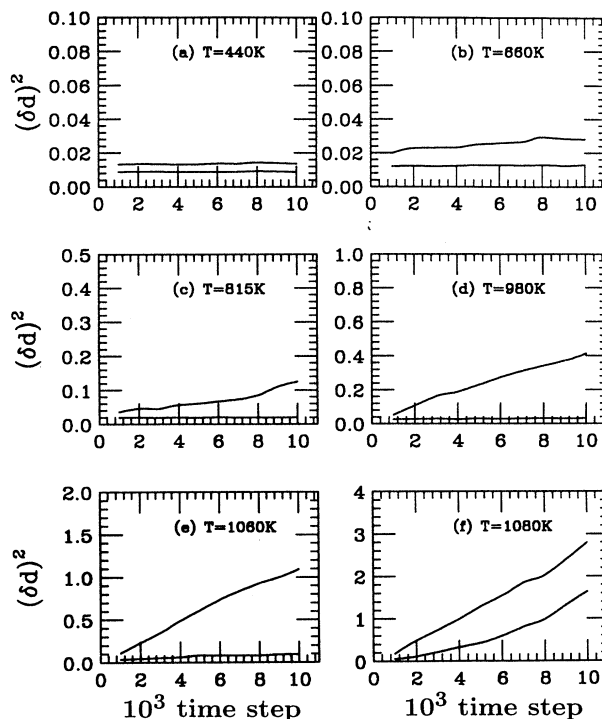


FIG. 3. The average mean-square displacement of surface atoms (upper curves) and bulk atoms (lower curves) for the  $N=725$  cluster at various temperatures. Here surfaces atoms are defined to be those which are initially at radii  $r > 4$  atomic spacings.

cluster. As shown in Fig. 2, these mean-square displacements  $(\delta d)^2$  are small and constant at low temperatures, but are (close to linear) functions of time at sufficiently high temperatures. However, below the melting temperature ( $T \sim 1080$  K), there exists a temperature range in which  $(\delta d)^2$  also shows a roughly linear, diffusive, dependence on time. This diffusive behavior in the solid phase is explained as a consequence of the motion of surface atoms which are less bonded than their bulk counterparts and are thus more easily activated. To demonstrate this, we separated the atoms in the cluster according to their distance from the center of mass of the cluster. In the data of Fig. 3, “surface atoms” are those which originally lie at radii  $r > 4$  atomic spacings from the center of mass, while the remaining atoms are classified as bulk atoms. As the temperature is increased, the surface atoms start to diffuse while the bulk atoms still remain near their equilibrium positions [see Figs. 3(a)–3(d)]. The bulk atoms do not begin to diffuse until the temperature is close to the bulk melting temperature. The same calculations were carried out on the clusters  $N=381$ ,  $177$ , and  $55$ . The  $N=381$  cluster shows behavior similar to the  $N=725$  cluster, but the  $N=55$  and  $177$  clusters did not show significant diffusion below their melting temperatures. The total diffusion constant (averaged) over all atoms is presented in Fig. 4. Clearly the diffusion constant of the  $N=381$  and  $725$  clusters is significant even below their melting temperatures, while that of the  $N=177$  cluster is quite small. For the  $N=55$  cluster

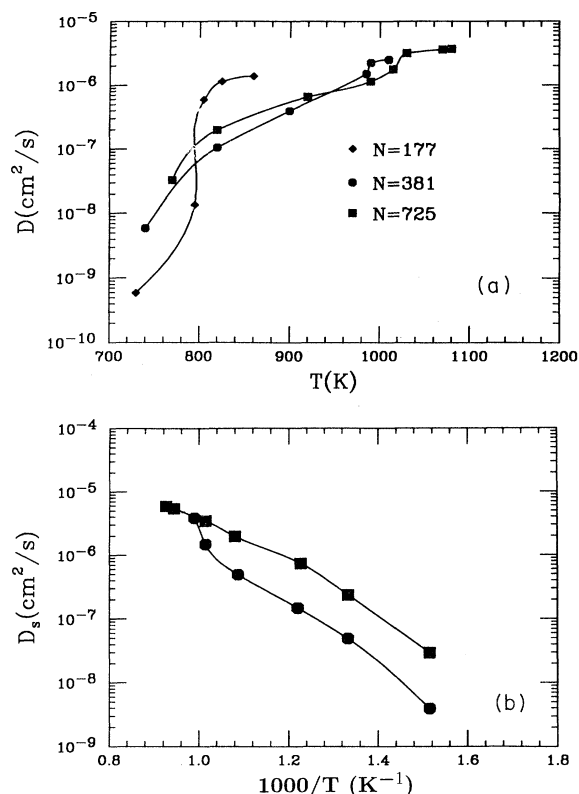


FIG. 4. (a) Estimates of the diffusion constant  $D$  (averaged over all atoms) found from data such as that in Fig. 3(b). A log- $1/T$  plot of the surface diffusion constant (only atoms with  $r > 4$ ) to test for activated behavior; the activation energy is roughly 0.1 eV.

(not shown in Fig. 4) the diffusion constant below its melting temperature was too small to be reliably calculated. For sufficiently small clusters, there is no real distinction between surface and bulk atoms, so it is not too surprising that surface diffusion below melting is absent for sufficiently small clusters. This absence of surface diffusion in small solid clusters leads to qualitatively different behavior in their nonequilibrium shape change dynamics, as we shall demonstrate below.

To study the kinetics of shape change from an initial nonequilibrium shape, we started with elongated fcc structures, and calculated the radius of gyration as a function of time. The radius of gyration is defined as

$$r_g^2 = \frac{1}{N} \sum_1^N [\mathbf{r}_i(t) - \mathbf{r}_c]^2,$$

where  $\mathbf{r}_c$  is the center of mass of the cluster. The initial state for an  $N=41$  cluster is shown in Fig. 5(a), while the late stage compact structure is shown in Fig. 5(b). For this cluster the initial elongated cluster is metastable for temperatures below the cluster melting temperature ( $T_m=480$  K). This is seen in Fig. 6, which presents  $r_g$  as a function of time for the  $N=41$  cluster at two temperatures. In the solid phase, only small fluctuations occur at short times, but after time  $t_c$ ,  $r_g$  suddenly decays to a

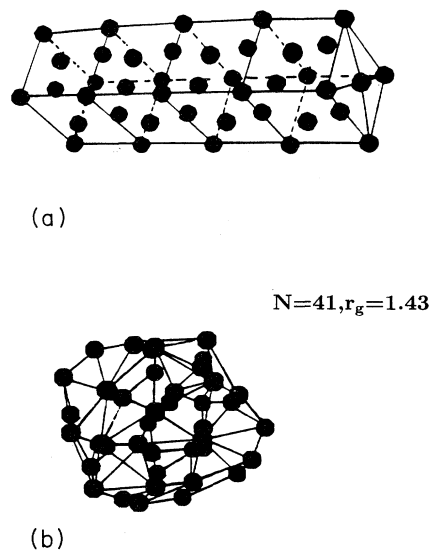


FIG. 5. (a) The initial fcc structure of an  $N=41$  cluster and (b) the compact shape found after 500 000 time steps.

lower value within a short time period  $t_q$  (about 5000 time steps). This abrupt decay behavior of  $r_g$  appears in small solid clusters. The value of the completion time  $t_c$  has very strong statistical fluctuations and depends very strongly on temperature, as is expected for a nucleation process. We tried to do a simulation at  $T=0.50T_m$ , but failed to observe any significant change in  $r_g$  even though the number of time steps exceeded  $1 \times 10^7$ .  $t_c$  also

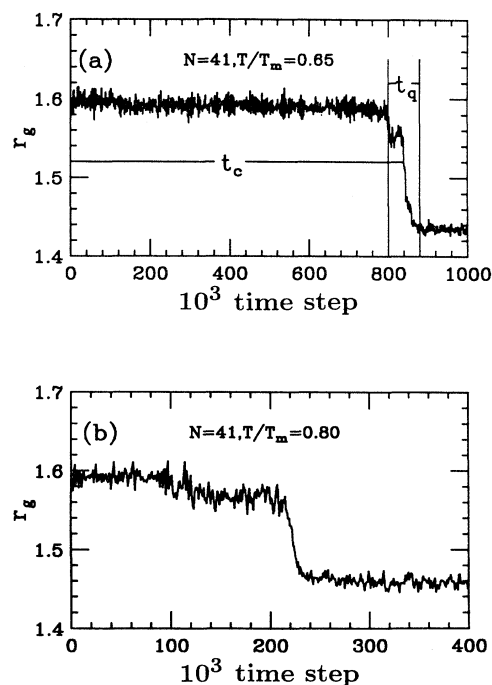


FIG. 6. The time dependence of the radius of gyration of  $N=41$  clusters at (a)  $T/T_m=0.65$  and (b)  $T/T_m=0.80$ .

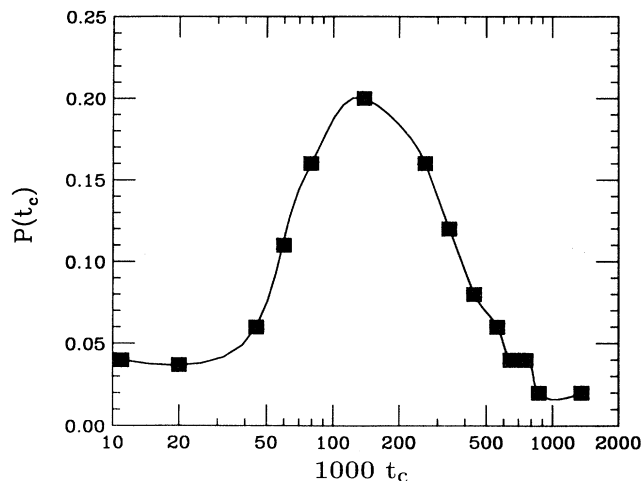


FIG. 7. The distribution of completion times for the  $N=32$  cluster at  $T/T_m=0.8$ .

depends strongly on the initial state of the cluster. To study these statistics in more detail, we studied the distribution of  $t_c$  for a cluster of 32 atoms at a temperature  $T=0.8T_m$  and found that the distribution is very broad. Figure 7 gives a linear-log plot of the distribution of  $t_c$ , and shows a well-defined peak near 150 000 time steps.

Calculations of the time evolution of  $r_g$  for larger clusters are shown in Figs. 8–11. The starting configurations are again elongated fcc structures. Figure 8 shows the decay of  $r_g$  for the cluster  $N=213$  at temperatures  $T/T_m=0.92$ , 0.95, and 0.98. An abrupt decay in  $r_g$  clear-

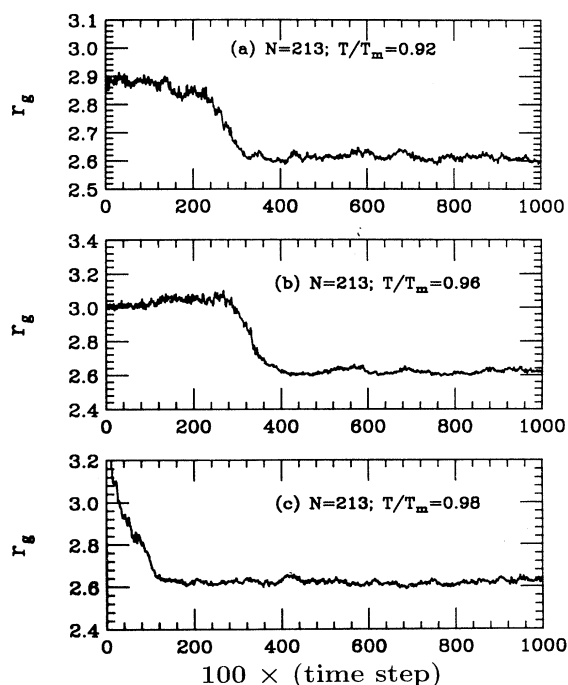


FIG. 8. The time dependence of the radius of gyration of an  $N=213$  cluster at various temperatures.

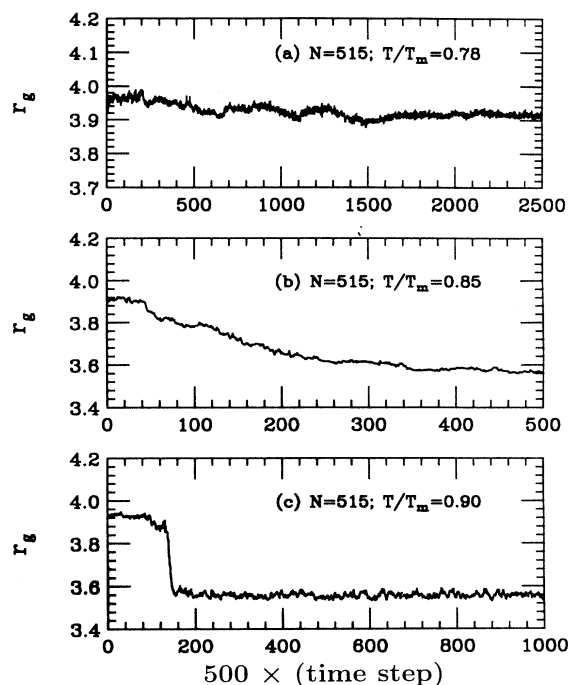


FIG. 9. The time dependence of the radius of gyration of the  $N=515$  cluster at various temperatures.

ly occurs at temperatures  $T/T_m=0.92$  and 0.95 and the behavior at  $T=0.98T_m$  is rather abrupt, but with a small nucleation time due the proximity to  $T_m$ . For the cluster  $N=515$  (Fig. 9),  $r_g$  decreases slowly and smoothly at

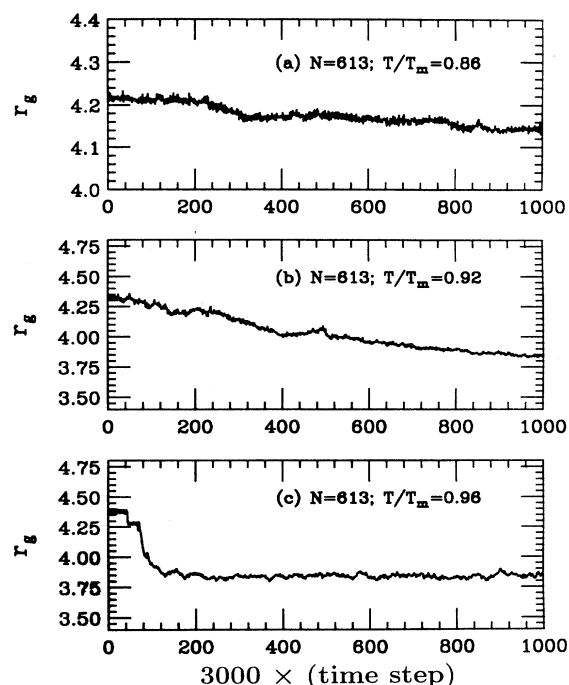


FIG. 10. The time dependence of the radius of gyration of the  $N=613$  cluster at various temperatures.

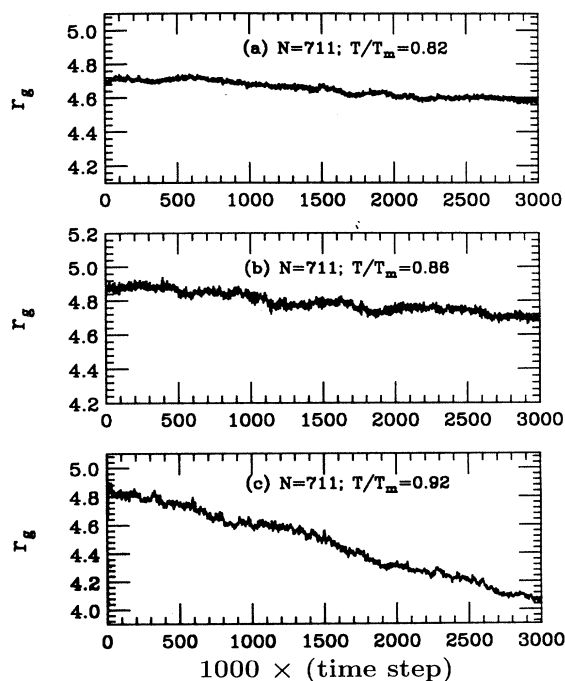


FIG. 11. The time dependence of the radius of gyration of the  $N = 711$  cluster at various temperatures.

$T/T_m = 0.78$  and  $0.85$ , while at  $T = 0.90T_m$ ,  $r_g$  has an abrupt decay near 75 000 time steps. A very similar decay behavior of  $r_g$  was seen in the cluster  $N = 613$  (Fig. 10). At temperatures  $T/T_m = 0.86$  and  $0.92$ ,  $r_g$  decays gradually compared with the rapid compactification at  $T_m = 0.96$ . For the cluster  $N = 711$  (Fig. 11), gradual decay behavior was observed at temperatures  $T/T_m = 0.82$ ,  $0.86$ , and  $0.92$ . We had difficulty in locating a temperature below  $t_m$  at which the decay of  $r_g$  in the cluster  $N = 711$  was abrupt. The data of Figs. 7–11 imply that there exist two kinds of decay mechanism in solid clusters. Small clusters, and large clusters near their melting temperatures, decay primarily by a nucleation process over a metastable barrier so  $r_g$  remains almost unchanged for a period of time before abruptly shrinking. At sufficiently low temperatures this activated process essentially stops, so small clusters are frozen in metastable states. Large clusters can still decay by surface diffusion, which is the dominant decay mechanism for a significant size and temperature range. These results are summarized in Fig. 12, which gives the region in which surface diffusion is the dominant mass transport mechanism (re-

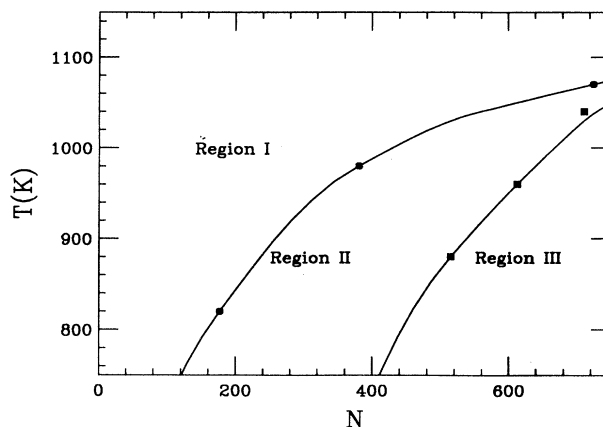


FIG. 12. A schematic of the regions in which clusters are melted (region I), clusters coalesce by abrupt shape change (region II), and where surface diffusion is the dominant coalescence mode (region III).

gion III), the regime in which a nucleation mechanism operators (region II) and finally the liquid phase (region I).

### III. SUMMARY AND CONCLUSIONS

For gold clusters of size greater than about 200 atoms there is a clear evidence for significant surface diffusion prior to the cluster melting temperature (see Figs. 3 and 4). For very small clusters, there is much less atomic diffusion below the cluster melting temperature.

Due to the absence of surface diffusion in small clusters, small solid clusters are easily frozen in anisotropic shapes, and only become compact by thermal activation. The cluster shape thus stays the same for a long time, and then abruptly changes to a more compact form. The distribution of completion times for this process is very broad as is expected for a nucleation process. In contrast, large clusters where surface diffusion may occur usually coalesce smoothly by surface mass transport. This is more like bulk behavior, where it is known that surface diffusion is dominant except on very long length scales and close to the melting temperature. The regimes in which these processes are dominant are sketched in Fig. 12.

### ACKNOWLEDGMENT

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