Experimental Evidence for Quasimelting in Small Particles

P. M. Ajayan and L. D. Marks
Department of Materials Science, Northwestern University, Evanston, Illinois 60208
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We present experimental evidence which demonstrates for the first time that small particles on substrates sit in deep potential-energy wells and, once floated out of these, can quasimelt between various local minima on shallow morphological free-energy surfaces. The energy needed to nucleate the quasimolten state is found to be orders of magnitude larger than that needed to sustain the state. The particles retain the unstable state for long intervals of time until they find another well on the substrate in which they can form a stable Wulff polyhedron shape.

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It has been demonstrated, both theoretically[1] and experimentally,[2] that small particles of many materials tend to form icosahedral, dodecahedral, and various multiply twinned states rather than their stable bulk structure. It has also been pointed out[3] that the configurational space of these small particles is densely populated due to their shallow free-energy surfaces[4] with a multiplicity of local minima. We have in the past[5] evaluated part of the Gibbs free-energy surface for small particles and the corresponding Boltzmann distributions and found that particles (size range of a few nanometers) can escape into a "quasimolten" state at low tempertures compared to their true thermodynamic melting points, due to the low activation-energy barriers between the various states. This and other theoretical results[6] were to some extent experimentally verified[7] when a small particle was found to fluctuate between various shapes under an intense electron beam, in an electron microscope, with frequencies of the order of 60 Hz/s. However, it has been suggested that the source of these fluctuations is violent events such as core excitations[8] or a Coulomb explosion;[9] the fluctuations being due to the particle recrystallizing from a highly excited, possibly molten state many times per second. A fundamental physical problem is which of these models is correct since experimental proof for neither exists so far.

The purpose of this Letter is to present experimental observation that although a large dose of electrons, and hence quite large amounts of energy, is needed to initiate the state in which a small particle sitting on a substrate

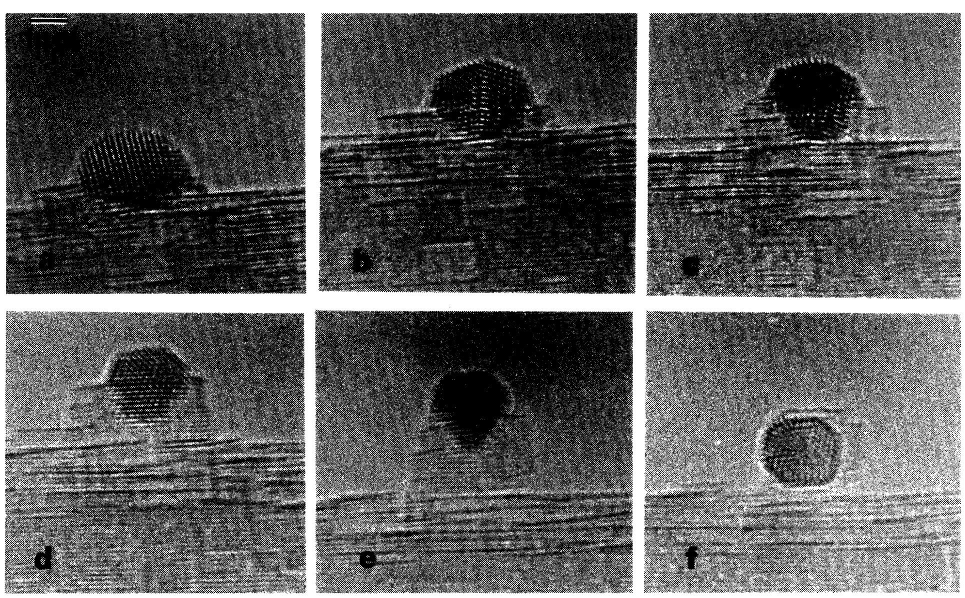

FIG. 1. Sequence of images showing a small gold particle on a MgO substrate changing, during electron irradiation, from a stable shape to the quasimolten phase. (a) Original particle (0 min); (b), (c), and (d) images after 60, 120, and 180 min of irradiation. The particle is slowly being encapsulated by the growing substrate overlayers; (e) the particle has been lifted off the original substrate layer, decoupled (220 min); (f) quasimelting state (240 min).

(trapped in a deep potential-energy well) starts fluctuating, the energy needed to sustain that state is orders of magnitude smaller. This is in agreement with our earlier prediction that a quasimolten state distinct from the thermodynamic molten state exists in small particles and appears to rule out the violent-event models.

Our experimental procedure involved dispersing gold clusters, prepared by the reduction of organometallic compounds,[10] onto magnesium oxide smoke particles which had been collected onto a copper grid by placing it over burning magnesium in air. The sample was then observed in a HITACHI-9000 high-resolution electron microscope, operating at an accelerating voltage of 300 kV. The specimens were clean without any amorphous-carbon support and the vacuum at the specimen area during microscope operation was approximately 10^{-7} Torr. During the whole operation no trace of any carbon contamination was found around the area of the specimen under observation. Figure 1 shows a small gold particle sitting on a MgO substrate, with a stable shape, evolving through the process of sinking into diffusing substrate overlayers,[11] decoupling from the substrate, and finally going into a state where it starts changing shapes between various twinned structures. The energy needed to initiate this unstable phase was provided in the form of high-flux electron-beam ($\sim$10–100 A/cm^2) irradiation for a long period of time. The final image [Fig. 1(f)], when the particle is in the quasimolten phase, is the ensemble average of many particle shapes which occurred during an exposure time of 3 s. The details of the particle morphologies that occur during these structural fluctuations have already been reported[7] and will not be repeated here. It is clear from the image that the original stable particle on the substrate has a large contact area (the formation of the interface reduces the free energy of the system), whereas in the fluctuating state the particle seems decoupled from the substrate with an almost spherical surface profile and a negligible area of interface. In some cases, the decoupling of the particle from the substrate takes another route. As seen from Fig. 2, the particle gets lifted off from the original substrate plane and moves to the top of a pillarlike structure that has grown from the substrate overlayers[12] before becoming unstable. The one-dimensional nature of the pillar suggests that the particle-substrate interactions have been reduced to a minimum and the conditions simulate that of a free-floating cluster in vacuum.

Since the theoretical predictions demanded only small activation-energy barriers between different particle morphologies in a small particle, a crucial question is, does it need such a high-flux electron beam to transport the particle between various states. We have observed that this is not true. It needs large amounts of energy to push the particle out of a large potential well in which the particle is trapped in as a familiar Winterbottom shape;[13] see Fig. 3 for the schematic. But, once initiated, the particle quasimelts even after the electron-beam intensity is turned down to almost zero. The fluctuations in the particle were observed at the lowest possible flux conditions in the microscope to see an image (using a TV intensifier with the gain on the intensifier at the maximum value), which corresponds to a flux of <0.1 A/cm^2. This unstable phase of a small particle persisted

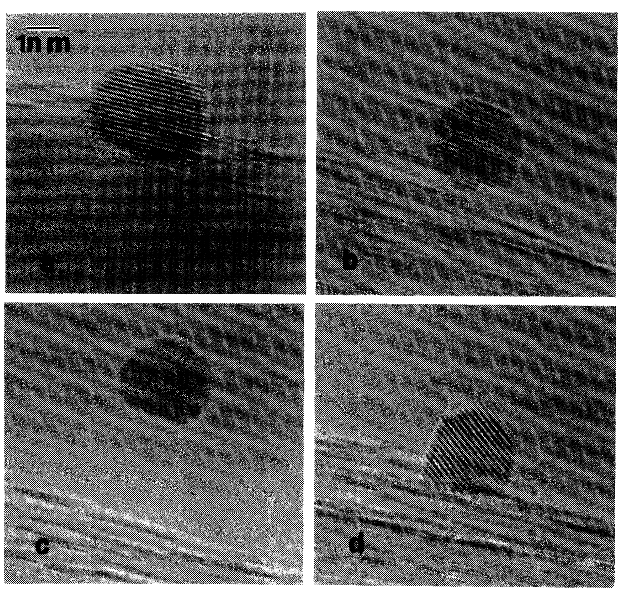

FIG. 2. A small particle of gold evolving under electron-beam irradiation. (a) Original particle (0 min); (b) just before being lifted off the substrate plane (230 min); (c) particle sitting on a pillar grown from substrate overlayers, quasimelting; (d) the pillar has partially collapsed and the particle fallen off onto the substrate and crystallized into a stable Wulff polyhedron with well-defined facets (270 min).

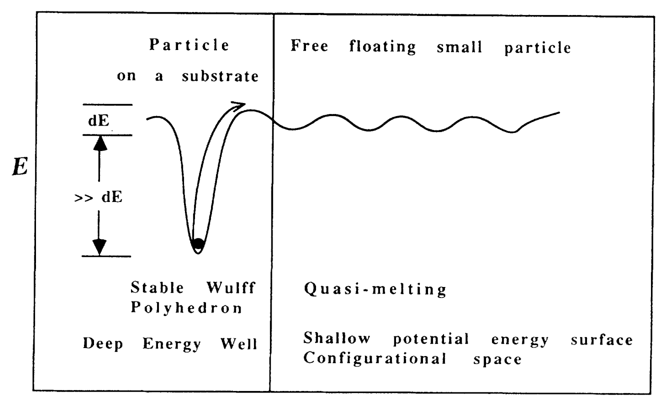

FIG. 3. Schematic showing the deep energy wells in which a small particle on a substrate gets trapped as a familiar Winterbottom shape. Once out of the well, the particle can hop easily over the shallow morphological potential-energy surface. Here b denotes the parameter that defines a particular configurational state.

for long times, a maximum of 40 min that we have observed so far. Even when the electron beam was completely turned off for about 5 min, and then turned on at the lowest flux for observation, the particle was still fluctuating. This means that either the particle was fluctuating when the beam was off or the activation energy needed to form the quasimolten phase in small particles is much lower than previously reported.[7] It was noticed that as the height of the pillar increased, the frequency of fluctuations of the particle increased suggesting that the stability in structure of the small particle decreases with decreasing interaction with the substrate. The particle became stable again only when it found another potential well on the substrate, as seen in Fig. 2(d), when the pillarlike structure partially collapsed and the particle crystallized on the substrate into a familiar Wulff polyhedron shape with well-defined surface facets.

These observations confirm our earlier predictions[5] on the free-energy surfaces and Boltzmann distributions in small-particle structures. A particle of any size should theoretically follow a Boltzmann-type distribution in the interval of infinite-time scales, due to the statistical fluctuations (order of kT) in the system. But, in small particles where the activation-energy barriers between various states are extremely small,[5] the dwell times of individual states could be small and the Boltzmann distribution could evolve in observable times. We have evaluated[5] the probabilities of these changes in particle morphologies and termed such an unstable state as quasimolten. We have, here, experimentally simulated conditions of an almost-free-floating cluster and demonstrated that the particle left to itself is unstable and random walks in configurational space between various morphological states.

Other possible causes of the quasimolten state are not consistent with our experimental results. A thermal origin for the process, which was reported elsewhere,[7,8] can be ruled out. Considering only radiative heat transfer from the particle to the surrounding, and using the Stefan-Boltzmann law for black-body radiation, we obtain[14] orders of milliseconds for the temperature to drop from near melting points to room temperature for MgO and gold particles for the sizes that we observe. Local melting and recrystallization[8] does not seem to be a viable route since at fluxes as low as we have reported, the frequency of structural rearrangements given by this model will be too low (we observe frequencies of 1–10 Hz for a 20-Å particle even at low fluxes). Energy gain through channels involving core excitation[9] could be possible but in that case the critical flux for such events should be much lower than previously reported. Since these excitations have decay times of less than fractions of seconds, the persistence of the unstable phase cannot be explained by the same model. These violent models are highly improbable since they are high-flux and hence low–cross-sectional events and need not be invoked for sustaining the quasimolten phase; as mentioned below they may play a role in initiating the quasimolten phase but not in sustaining it.

The way the electron beam deposits energy into a small particle through electronic excitations is not clear as yet. We have found that the large amounts of energy needed goes to break the bonds at the particle substrate interface and free the particle from the potential well, and this could involve violent electronic excitations. Charging of the particle or the MgO does not seem to be taking place since this would have created problems in imaging, which was not observed. The fact is that the energy fluctuations due to the smallest number of electrons that can be used for imaging in an electron microscope are enough to make the particle structurally unstable; indeed, we suspect that, in the absence of the beam, the particle is quasimolten although, of course, we cannot prove this. An increase in the mean energy (thermal or electronic) may increase the system fluctuations. It has been observed that when the electron flux is increased the particle starts changing shapes at a faster rate, essentially flattening the Boltzmann distribution.

The results we present here are clear experimental proof for the existence of a quasimolten phase in a free small particle. The stable particle morphologies that one finds in experiments are the trapped morphologies in deep potential-energy wells on the substrate. The amount of energy needed to float the particle out of the well will depend on the strength of short-range interactions that stabilize the particle/substrate interface. But this energy is orders of magnitude higher than that needed to sustain the quasimolten phase in small particles.

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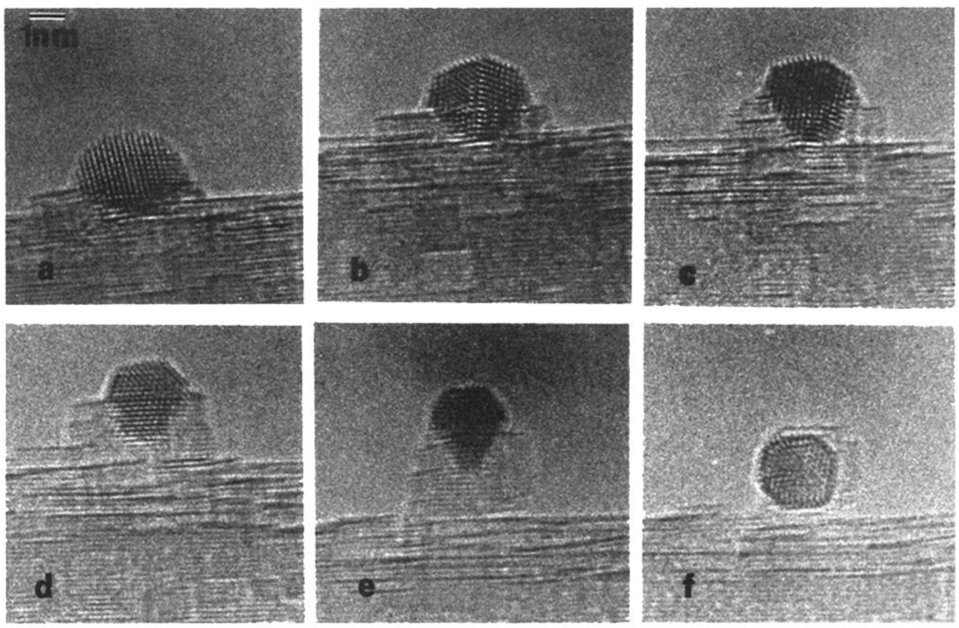

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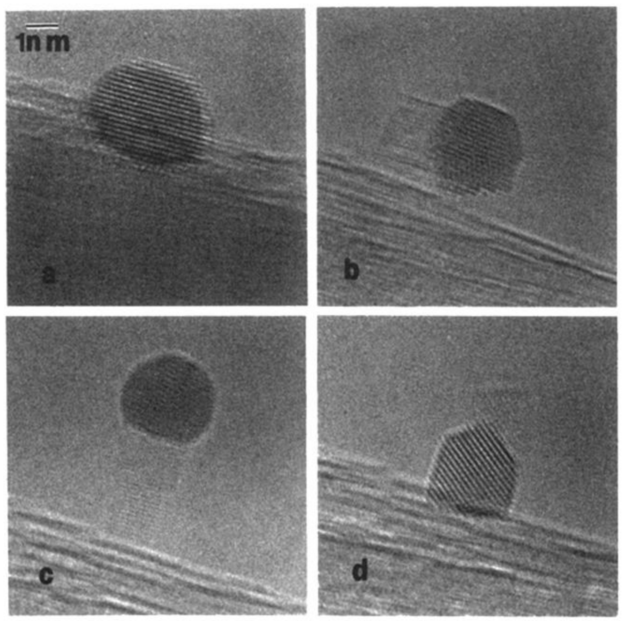

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