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Experimental studies of small particle structures

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Abstract

Data on the experimental structure of small particles is reviewed, the emphasis being an attempt to correlate experimental information with theoretical models. First, a general discussion of some of the controlling factors is presented, primarily equilibrium shapes of small particles, the effect of surface stresses, kinetics, and the role of chemisorption and the substrate. Experimental techniques for obtaining information about small particles are then described, primarily electron microscopy approaches. Experimental data on the static structure of small particles is then reviewed, both single crystals and the many, complicated twinned structures in face-centred cubic materials. An overview is then given of some of the more recent results on dynamic phenomena in small particles. Finally, a general model merging thermodynamic and kinetic factors is presented to attempt to rationalize the available data, followed by a brief discussion.

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1. Introduction

The structure of small particles is a topic which has fascinated scientists for more than a century. Many fundamental issues are involved: for instance, at what size does a small particle behave like the bulk material, for exaple, changing from an insulator to a semiconductor with quantized electronic levels? In addition, small particles play a significant role in many technologically important areas such as heterogeneous catalysis, as well as in emerging areas such as fullerenes, nanomaterials and quantum dots. The range of publications on small particles is similarly immense, spanning cluster chemistry through particulate analysis for pollution control. Almost every possible physical or chemical probe has been used, with varying degrees of success.

It is not possible here to cover this very large field completely, and almost inevitably even a partial review will overlook papers. The focus of this review will be primarily upon the atomistic structure of small particles in the 1–100 nm size regime, primarily the fcc metals since these have been by far the most widely studied. Even within this more limited area, it is not possible to review the field fully since, due to the diversity of the publication sources, it suffers from duplication of results. The majority of the description will focus around electron microscopy data since this is the most informative experimental technique, although data from a few other techniques will also be included.

It is also the belief of the author that small particle structures cannot be understood purely from experimental data, and it is necessary to simultaneously use theoretical or other modelling. The prime reason for this is that electron microscopy produces images, and without models or hypotheses to test the data against it is difficult if not impossible to know what data is meaningful, what is not, or even start to rationalize why certain types of data are not so useful. This will be reflected here in that discussion of theoretical models will often be combined with the experimental results, and in many cases an attempt will be made to link quite disparate experimental and theoretical data.

The general conclusion that the author has formed by analysing the literature for this review is that there has been some fairly substantial progress over the last ten years with agreement about some aspects of small particle structures. At the same time a completely new area has opened up where the dynamic behavior of small clusters has replaced the static structure as the forefront of research. This seems to be the case both at the very small size scale, and for rather larger particles, and there are signs of consistency emerging between models appropriate for atomistic clusters of only a few atoms and those which can more readily handle large particles. Some other general reviews of experimental information about small particles can be found in volume 24 of Phase Transitions (1990), the PhD theses of Wallenberg (1987), Ajayan (1989), Flueli (1989), Hall (1991) and Malm (1991), and a review of Japanese work in this area has been presented by Uyeda (1991).

Before getting into the primary science, some general comments are important to try and set the tone of this paper. It might be thought that the question of the 'structure of small particles' should be one which is amenable to a relatively simple answer; for a particular material at a given size one might have structure 'A' which changes to 'B' as the size increases (e.g. a first-order phase transition) with the two structures A and B functions of the material and conditions. Sometimes this is true, but quite often it is far more complicated than this. The reason is that structures in general, not just small particles, are history dependent and involve both kinetic and thermodynamic factors. In the most general case what is found is a mixture of different structures at any given size which, as will be discussed later, represents the *statistical* thermodynamics of the energies of different structures, plus the effects of kinetics during the growth process effecting a

population of structures in a complicated and multi- dimensional phase space. Because of this it is possible to be trapped asking the wrong type of question about small particles. One particular example of this is very common in the literature, and relates to complicated structures called multiply-twinned particles or MTPs (discussed later) which are often found at very small sizes. Many authors have looked into the question of the energies of MTPs relative to simpler single crystals, and have calculated sizes above which these particles are thermodynamically unfavoured. There is nothing wrong with doing this, but making correlations between this type of analysis and the presence or absence of these twinned structures in experimental data makes so many assumptions about the kinetics that in can be simply bad science. A more important point is that attempting to force experimental data to fit or test a preconceived model prejudices how experimental data are published.

The general structure of this review is as follows. I will start with a general description of some of the thermodynamic and kinetic factors which influence particle structures. This is then followed by a general description of the primary experimental probes, chiefly electron microscopy based techniques. The static structures of a number of different types of small particle structures are then discussed, followed by non-static structures or dynamics. Finally, I will return to some of the ideas of kinetics versus thermodynamics discussed above to try and pull together some of the results, concluding with a brief discussion.

2. Background thermodynamics and kinetics

2.1. Surface energies and the Wulff construction

The surface energies of different facets play a central role in the energetics of small particles. For any given surface, the free energy per unit area is commonly described by a free energy function of the form $\gamma(\theta, \phi)$ where θ, ϕ are polar coordinates describing the surface normal. The total surface free energy of the particle can then be written as:

$$G = \int \gamma(\theta, \phi)\, \mathrm{d}A \tag{1}$$

where the integral is over the surface, or in the equivalent form for a facetted particle

$$G = \sum_i G_i = \sum_i \gamma_i A_i \tag{2}$$

where the i subscript represents a particular surface facet of area A_i.

The minimum energy shape for a given volume is determined by the Wulff construction, named after the author of some of the very earliest experimental work on equilibrium shapes (Wulff 1901). Solved partially by Hilton (1903), Liebmann (1914) and Laue (1943), a more complete and general proof was first provided by Dinghas (1943) although it is more common to refer to the work of Herring (1952) as a source. Representing the surface free energy as a function of direction by vectors of length γ_i as illustrated in figure 1, the minimum energy shape at constant volume is the inner envelope of the normals to this surface. This construction gives the equilibrium shape of a free-floating small particle, and is mathematically equivalent to stating that the normal distance from a common centre to any given surface facet is proportional to the surface free energy of that facet. The most convincing verification of the Wulff construction is the work of Heyraud and Metois

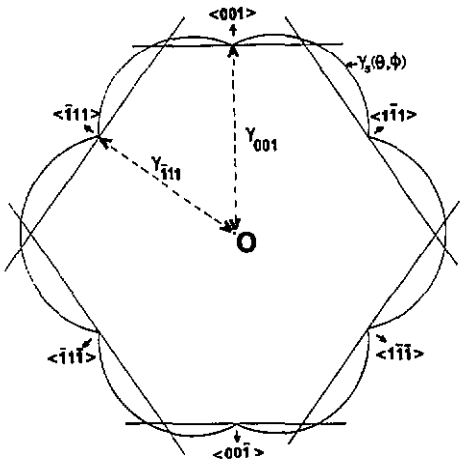

Figure 1. Schematic diagram of the Wulff construction in two dimensions for a {110} section of an fcc single crystal. The inner envelope of normals to the surface free energy as a function of direction is the lowest energy single crystal structure. The example shown would lead to only {111} and {100} facets; other facets are possible with a different directional dependence of the surface free energy.

(1983). These authors demonstrated that for micron sized particles equilibrated with their own vapor, the morphology is independent of the actual size.

Although the Wulff construction is the correct equilibrium shape for large (single crystal) particles which can be treated as continua, it need not be correct for much smaller ones. For instance, it neglects edge and corner energies which may be important at smaller sizes; Wang *et al* (1984) suggested that this could stabilize irregular polyhedra over simpler morphologies. There is a second effect at small sizes which can be very significant, and is due to the discrete nature of atoms (Marks 1985a). In a continuum model the volume should be taken as the multiple of some constant and a characteristic length of the particle cubed, the total surface energy as the contribution which scales as the same characteristic length squared and so forth for 'edge' and 'corner' energies. Note that the 'edge' energy contribution is not simply proportional to the number of edge atoms. To illustrate this, consider a simple octahedral fcc particle with only (111) facets, where the number of atoms along the (111) facets is n. From simple counting

$$\begin{aligned}&\text{Total number of atoms} = n(2n^2+1)/3\\&\text{Atoms on (111) faces} = 8((n-1)(n-4)/2+1)\\&\text{Atoms on edge} = 12(n-1)\\&\text{Atoms at the vertices} = 6.\ cr\end{aligned} \tag{3}$$

We can take the characteristic length to be proportional to n. Taking, for argument, the cohesive energy per atom as $-\varepsilon$, the excess energy of an atom on the (111) faces as $\varepsilon/3$, and the excess energy of an edge atom to be $\varepsilon/2$, the effective edge energy term (the term which scales with n) is $-n\varepsilon$ which is negative; the effective edge contribution reduces the particle energy rather than increasing it. This leads to surprisingly large deviations from the Wulff construction even at quite large numbers of atoms, as shown in figure 2. Another problem is that higher index facets may not be able to fit on a small particle; for a continuum model to be relevant the dimensions of all surface facets should be much larger than the unit cell of the surface facet.

A number of experimental analyses have shown that single particles in the tens of nanometer size range are generally consistent with a Wulff construction (Wang *et al* 1985, Flueli and Borel 1988, Marks and Ajayan 1990). One analysis as a function of particle size shown in figure 3 (Bonevich 1989, 1991) does indicate a size dependence. A strong

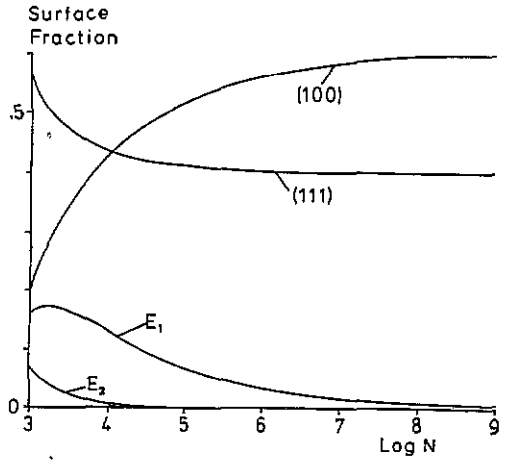

Figure 2. Variations in the number of atoms of different types obtained using a discrete atomic model with the energy of every surface atoms the same, taken from Marks (1985a). The curves marked (100) and (111) correspond to the number of atoms on these two faces respectively, E_1 and E_2 two different types of edge atoms.

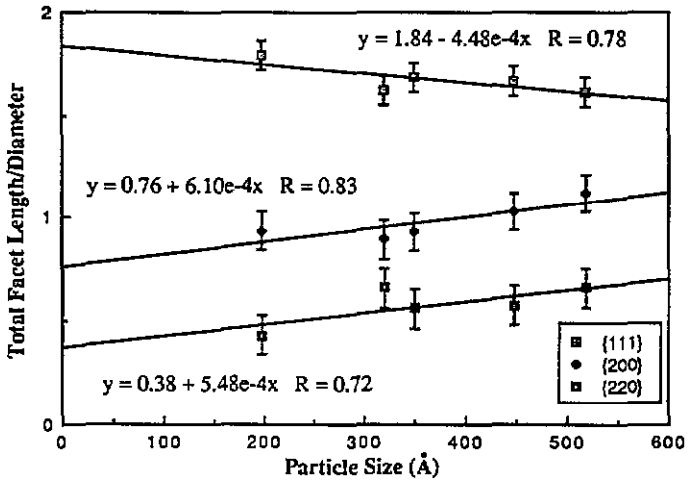

Figure 3. Plot of the total facet size scaled by the particle diameter for small alumina particles, taken from Bonevich (1989, 1991), with straight line fits and confidence levels shown. Although the number of data points is small, it clearly indicates an increase in the (111) facets at the expense of (200) and (220).

variation in the faceting as a function of size has also been observed in calculations by Cleveland and Landman (1991).

An important extension of the Wulff construction was made by Winterbottom (1967) for a small particle on a rigid substrate. He showed that the role of the substrate can be included by modifying the Wulff construction, changing the free energy of the contact plane by adding in a component for the free energy of adhesion as illustrated with an experimental example in figure 4. This can be extended if the substrate is not rigid but also allowed to change its morphology (Marks and Ajayan 1990). There are also a number of other effects

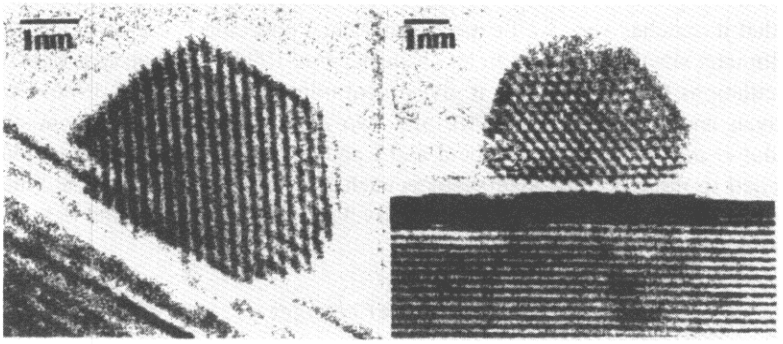

Figure 4. Experimental image of two small gold particles on an MgO substrate, taken from Ajayan (1989). Note the increased cross-section at the particle-substrate interface.

that can occur due to elastic deformations at the contact plane (Johnson *et al* 1971, Chaudhri and Yoffe 1981, Easterling and Tholen 1972, Tholen 1986, Demejo *et al* 1988, Bowen *et al* 1989, Rimai *et al* 1989, 1993). However, excepting the work of Tholen and co-workers for metals there appears to be no reports of this in small particles and such phenomena were not observed in small particles of alumina (Bonevich and Marks 1992), although this is not too surprising considering that ceramics such as alumina have far higher elastic constants than metals. At the present moment it is not very clear how important these elastic deformations are in small particles.

2.2. *Modified Wulff construction*

The standard Wulff construction deals with a single crystal, and in the approach of Winterbottom (1967) can include the effect of a substrate. As will be seen later, it is very common to find particles containing twin boundaries. An extension of the Wulff construction was proposed by the author (Marks 1983a, 1984), and works very well in explaining many of these structures. A composite particle is conceptually separated at the twin (or other) boundaries, and the free energy per unit area of the boundary partitioned in some fashion into two components α and $(1 - \alpha)$. The surface free energy of each component can be minimized directly, and is a Wulff construction with the boundary energy terms included in the same sense as used for a substrate. Each part of the resulting shape satisfies the condition for the Wulff construction, so a stationary point, i.e. a minimum, maximum or saddle point of the total free energy is obtained by rejoining the separate segments, with the constraint that they must fit together properly without any exposed surface of the boundary; the character of the stationary point is determined by the change in energy as a function of the parameter α.

In two dimensions or with a completely isotropic surface free energy it is easily shown that the construction only yields a saddle-point. This need not be the case with a three-dimensional facetted particle, but checking the sign of the second derivative is hard. It is possible to argue on physical grounds that this construction will often lead to a local minimum in energy. There is a driving force to move the internal boundary out of the particle, but the only way to move it away from the stationary value is to introduce distortions of the outer surfaces. Since the energies (per unit area) of these outer surfaces are typically much larger than that of the internal boundary, this may require a net increase in energy. Note that the construction gives a morphology which is a local, but not necessarily the global minimum, energy configuration.

At the present moment, 'proof' of this 'modified Wulff construction' is only available in that it matches very well experimental data, particularly for MTPs (Marks 1984), even for millimeter sized twinned particles (Haluska *et al* 1993). For one type of MTP direct numerical calculations have shown that it gives local minima (Marks *et al* 1986, Dundurs *et al* 1988, Ajayan and Marks 1988, 1990), and two analyses based upon atomistic calculations by Raout *et al* (1989) and Cleveland and Landman (1991) support its validity. It can also be applied to more complicated systems such as particles on a substrate when the substrate is allowed to deform, and at least qualitatively explains experimental data (Ajayan and Marks 1989a, Marks and Ajayan, 1990).

2.3. Surface stress and lattice parameter changes

In many cases small particles are subjected to substantial strains which may lead to appreciable effects. The conventional approach is to consider both an area change and a change in the surface free energy, in which case one can write for small strains e_{jk}

$$G_i = \gamma_i A_i + \sum_{jk} e_{jk}\sigma^i_{jk} \tag{4}$$

where σ^i_{jk} is the surface stress tensor for the i face and has the form (Herring 1951)

$$\sigma^i_{jk} = \gamma_i + \partial\gamma_i/\partial e_{jk}\,. \tag{5}$$

The physical interpretation of the surface stress tensor is as follows. When a new surface is created and assuming no reconstructions, atoms in the plane of the surface are constrained by the underlying bulk to retain their in-plane periodicity. If this constraint was not there, they could relax their in-plane spacings. The derivative of this energy change with respect to various types of strain is the surface stress tensor.

The existence of a surface stress tensor term is now widely accepted. For instance, as first suggested by Herring (1951), it can directly lead to surface reconstructions and his original models are remarkably similar to many known surface structures such as the Si (111) 7×7 (Takanayagi *et al* 1985a,b) and gold (111) 23×1 surfaces (Tanishiro *et al* 1981). The idea of surface stresses as the driving force or at least a strong influential factor in surface reconstructions has been shown both experimentally by Men *et al* (1986) and theoretically, e.g. Needs *et al* (1991). The most common approach to measure the surface stress tensor is to use the change in lattice parameter (e.g. Boswell 1951, Mays *et al* 1968, Solliard and Buffat 1977, Solliard 1983, Solliard and Flueli 1985, Multani *et al* 1990) as a function of size in small particles. The physical basis of this effect is that the total energy of the particle can drop by reducing (or increasing) by an elastic strain the area of the surface, this energy gain being balanced by internal strains within the particle. This is equivalent to the capillary pressure in a liquid drop, and leads to a change in the lattice parameter a of

$$\Delta a/a = -2\langle\sigma\rangle k/3r \tag{6}$$

where k is the bulk modulus and $\langle\sigma\rangle$ represents an appropriate mean over the particle surface. A good review of some of the earlier results can be found in the article by Linford (1973). This equation strictly holds only for spherical particles, and as pointed out early by Herring (1952), quite different effects occur with other shapes. In particular, when there are sharp facets on the particle the effect of the surface stresses is equivalent to applying forces

at the edges of the particle. (The distortions described by Herring are in fact remarkably similar to what is observed in small square pyramidal particles, see figure 8 later.)

The existence of changes in the lattice parameter in electron or x-ray diffraction patterns which scale inversely with the particle size is exceedingly well documented, although there is substantial scatter in the results. In general the lattice parameters are reported to contract, but there are exceptions such as the work of Oshima and Harada (1984) who report no change and Onodera (1992) who reports an expansion. The problem is that there are a number of experimental factors which have rarely been controlled. Almost all the experiments were performed (a) with supported substrates and (b) under vacuum conditions where the surfaces must be considered as contaminated. Experimentally, some impurity controlled value of σ is being measured, and since surface reconstructions are well known to change rapidly with contamination it is not impossible for the sign of σ to change. It should be noted that there is ample evidence (see below) for very large effects of contamination/chemisorption on surface free energies. (Even such an apparently inert material as gold does not exhibit reconstructed surfaces when contaminated.) There will also be a change in the lattice parameter due to an epitaxial substrate as shown by Vincent (1968) and Heinemann *et al* (1983), and there is no reason to ignore this effect even with an amorphous substrate.

In addition, simply measuring the central location of a diffraction ring is very dangerous. It is very well established in the electron microscopy/diffraction literature that determining spacings at the level of a few percent precision from small, inhomogeneous regions requires very careful work. As one specific example, in rigorous simulations Hall (1991) observed an apparent lattice parameter contraction in small icosahedral particles with particle size when there was, in fact, no change in the interatomic distances. It is only for a translationally periodic particle that there is a direct correlation between peak locations in a diffraction pattern and lattice parameters (Hall 1993, private communication).

Finally, many of these observations have assumed that the particles are single crystal spheres. Aside from the complications with non-spherical shapes mentioned above, there is no *a priori* reason why they should be single crystals. In fact, most of the studies have used gold or silver which are certainly not 100% single crystals, but instead contain significant numbers of multiply-twinned particles. As will be discussed later, these have intrinsic stresses which will destroy the validity of the interpretation, as well as not having translational periodicity.

More recently a number of theoretical calculations of the surface stress tensor have appeared (e.g. Needs 1987, Vanderbilt 1987, Meade and Venderbilt 1989, Wolff 1990). These, in general, indicate that clean surfaces are in tension, i.e. that the in-plane atomic spacing would like to contract.

To summarize, the surface stress term is important in small particles, both in terms of lattice parameter changes and energetically, particularly for multiply twinned particles as will be discussed below. Although the experimental data strongly supports a contraction, to what extent this is intrinsic or a consequence of surface contamination and interfacial stresses from the substrate is unclear. In the view of the author there is a need for some very careful experimental work addressing the effects of substrates and contamination.

2.4. Kinetic shapes

Although thermodynamics play a critical role, kinetics are often critical in small particle structures. One standard result is the difference between kinetically controlled structures produced by, for instance, evaporation and thermodynamic structures, as most clearly demonstrated by Metois *et al* (1982) for lead. During evaporation, particularly at lower temperatures, growth rates are controlled by the sticking probability on a given face. Since,

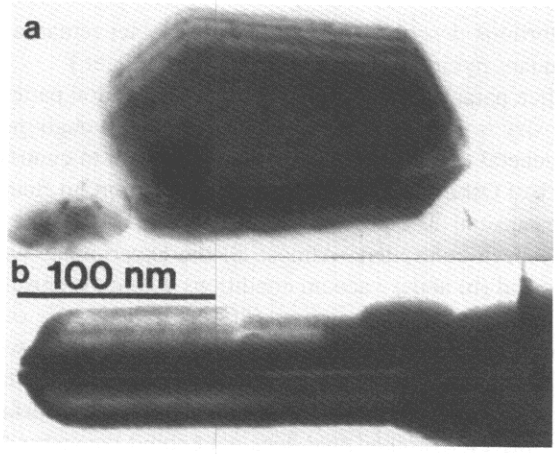

Figure 5. Images of a rather large platelet in (*a*) and needle in (*b*) in a silver catalyst sample on α-alumina, taken from Marks and Howie (1979).

Table 1. Relative surface areas of spheres of platinum after different types of treatment, taken from Flytzani-Stepanopoulos *et al* (1977).

Plane	Annealed	NH_3 Decomposition	C_3H_8 Oxidation	CO Oxidation
(111)	0.075	0.11	0.52	0.2
(100)	0.005	0.12	0.48	0.16
(421)	—	0.75	—	—
(310)	—	—	—	0.64
Curved	0.920	0.02	—	—

for instance, a (001) face of an fcc material has a higher sticking probability being of higher surface free energy than a (111) face, it will grow faster. The kinetic structure will therefore be dominated by slower growing faces such as (111), and might contain no (001) facets. Many of the early data on multiply twinned particles, for instance, show this phenomena, particularly the decahedral particles, as will be discussed later.

There are also certain special types of particle morphologies that occur when there is very strong kinetic control of the growth, for instance needles, platelets and dendrites, examples of the first two being shown in figure 5. The basic science of kinetic control of growth is quite well known, and can be found, for example, in the book by Tiller (1991). For the sake of completeness it is worth pointing out that needle-like structures can in fact be found in stable ligand complexes; for instance $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{15}(CO)_{30}]^{2-}$ both contain linear helical arrangements of Pt_3 triangles (Calabrese *et al* 1974).

Because of the role of growth kinetics, it is worth mentioning here a point that will arise again later; just because a particular morphology is observed does not mean that this is a thermodynamically stable structure. Instead it may correspond to a structure which at a very small size was stable or metastable, and just grew to a large size.

2.5. Role of surface chemisorption and the substrate

One of the trickiest issues in small particle research is surface cleanliness, and how this effects structures. It is exceedingly well established that chemisorption has a very dramatic effect upon surface energies, and will therefore also alter the equilibrium shape. A very nice demonstration of this can be found in the work of Flytzani-Stephanopoulos *et al* (1977); some of the data is summarized in table 1. These authors performed scanning electron microscopy analyses of spheres of Pt after their use as catalysts for NH_3 decomposition,

C_3H_8 oxidation and in CO oxidation. The initial spheres prepared at high temperature were highly curved, and developed into very facetted shapes during the treatments. One of their most dramatic results is that CO oxidation led to a 64% coverage of the surface by (310) facets; under no other conditions were these facets stable. Some more recent observations by Yanase *et al* (1990) have demonstrated that such effects are important at small sizes. These authors observed a reversible change in the lattice parameters of small silver particles using *in situ* x-ray diffraction between hydrogen in helium and oxygen in helium conditions. Experiments performed under scrupulously clean ultra-high vacuum conditions are rare, and even when the vacuum is adequate it is unclear whether the surfaces of the particles were rigorously clean.

The exact role of the substrate is also often obscure. In addition to a change due to the substrate–particle interface, there will always be interfacial stresses. In certain experiments deliberately encapsulated particles have been used to prevent atmospheric contamination, but this only changes the surface species from residual background gases to the elements in the film. It is also normally assumed that the substrate is completely rigid and does not change. Experimentally, this is not always the case. One particularly striking example of this is for small gold particles on MgO where the particle sinks into the substrate (Ajayan and Marks 1989a, Marks and Ajayan, 1990) as shown in figure 6; such phenomena will occur thermodynamically if the surface energy of the substrate plus that of the particle–substrate interface is somewhat less than that of the particle.

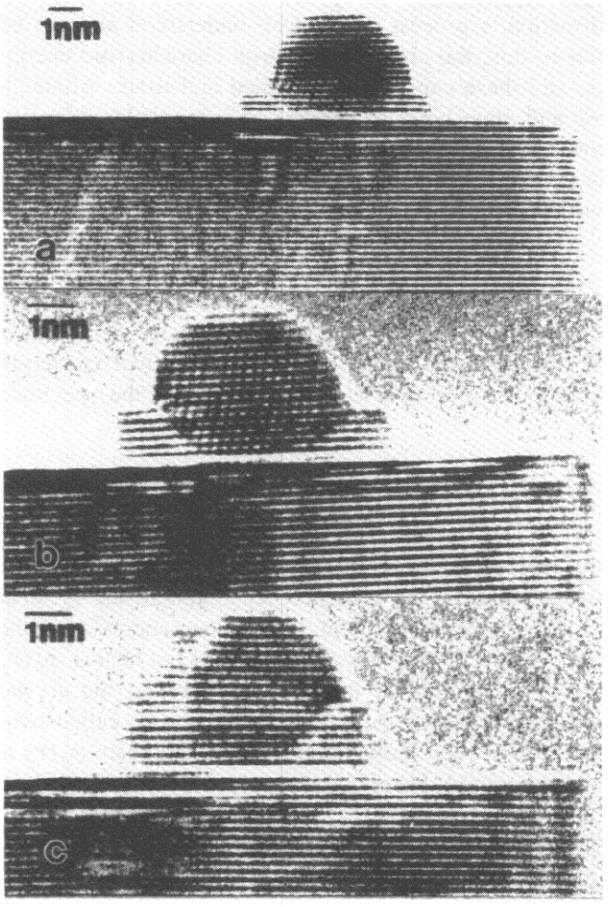

Figure 6. Time evolution of a small gold particle on MgO, (*a*) original; (*b*) after 10 minutes and (*c*) after 60 minutes. The MgO migrates to encapsulate the particle, because the appropriate sum of surface free energy of MgO and that of the MgO-gold interface is lower than that of gold.

The ideal experiment is to analyse the particles without a substrate. Although there have been a number of attempts to use electron diffraction on cluster beams as discussed in more detail below, to date it has not proved possible to fully determine the structure by these techniques. It needs to be appreciated that many of the experimental results described in the following sections may be strongly influenced by surface contaminants.

3. Experimental techniques

There are numerous techniques which have been applied to determine the structure of small particles over the years; in fact it would be fair to state that every possible spectroscopic and imaging/scattering tool has been used. For simple single crystals, most of these work fairly well. However, whenever the particles are complicated or the general morphology is not well characterized by other techniques, most fail. The most common technique is electron microscopy, and some of the basic techniques will be described here; except for relatively minor improvements these have been relatively stable over the last few years.

3.1. Electron microscopy

Electron microscopes use electron beams in the energy range of 100–500 keV transmitted through the particles to produce images or yield spectroscopic information. The scattering process is dynamical or multiple diffraction, a process that is well understood and can be calculated quite precisely. In addition to this, the electrons can lose characteristic energy quanta to excitations in the particles, and these can also be detected and used. Although these excitations lead to some heating and other types of damage, in general this is a very small effect as will be discussed below. Some general background specific to small particles will be detailed here; a comparison of the utility of various different techniques for obtaining structural information about small particles can be found in Howie *et al* (1982) and Marks and Smith (1983a).

3.1.1. Conventional dark-field and bright-field imaging. Even at the relatively high energies used in electron microscopy, the scattering process is completely dominated by multiple scattering effects and should not be approximated by a single or kinematical scattering analysis, unlike x-ray or neutron diffraction. The total electron wave after the specimen (small particle) has the general form

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{g}} \phi_{\boldsymbol{g}}(\boldsymbol{r}) \exp(2\pi i[\boldsymbol{k}+\boldsymbol{g}]\cdot\boldsymbol{r}) \tag{7}$$

where the vectors $\boldsymbol{g}$ are those of the reciprocal lattice of the particle, $\boldsymbol{k}$ is the incident electron wavevector and $\boldsymbol{r}$ is a position vector in the plane perpendicular to the incident electron beam. In general only those reciprocal lattice points almost perpendicular to the electron beam have any appreciable intensity. The amplitude of the diffracted beams, $\phi_{\boldsymbol{g}}(\boldsymbol{r})$ depends strongly both upon the relative orientation of the incident beam to the crystal lattice, and on the thickness. A good approximation to its behavior is the so-called two-beam approximation (e.g. Hirsch *et al* 1977), where only a single diffracted beam $\phi_{\boldsymbol{g}}(\boldsymbol{r})$ is considered together with the incident (transmitted) beam $\phi_0(\boldsymbol{r})$:

$$\phi_{\boldsymbol{g}}(\boldsymbol{r}) = \mathrm{i}(2meV_{\boldsymbol{g}}/h^2k)\exp(-\pi \mathrm{i} s t(\boldsymbol{r}))\sin[\pi s^{\mathrm{eff}} t(\boldsymbol{r})]/s^{\mathrm{eff}} \tag{8}$$

$$\phi_0(\boldsymbol{r}) = \exp(\pi \mathrm{i} s t(\boldsymbol{r}))(\cos[\pi s^{\mathrm{eff}} t(\boldsymbol{r})] - (\mathrm{i}s/s^{\mathrm{eff}})\sin[\pi s^{\mathrm{eff}} t(\boldsymbol{r})]) \tag{9}$$

where $t(\boldsymbol{r})$ is the local thickness and

$$s^{\text{eff}} = (s^2 + (2meV_g/h^2k)^{-2})^{1/2} \tag{10}$$

s being the excitation error (the distance between the sphere through the origin of the reciprocal lattice of constant radius k and the particular reciprocal lattice vector $\boldsymbol{g}$, taken along the electron beam direction) and V_g is the appropriate Fourier coefficient of the crystal potential. The same equation can also be used for x-ray or neutron diffraction, although in these cases the second term in the last equation is very small and can normally be neglected. For a more complicated case with more than one diffracted beam the qualitative results correlate to simply adding terms of these equations, although the detailed variations of amplitudes with beam direction and thickness are more complicated than this. (The more general case with many different diffracted beams active is quite well understood and can be calculated quite accurately. However, to date the additional information that is available has not been usefully exploited to obtain information about small particles, and will therefore not be discussed here.)

Depending upon how apertures and beam deflectors are used in the microscope, it is possible to obtain a variety of different types of images. The simplest form is to use an objective aperture that only allows a given diffracted beam through, and then obtain an image with this. If the beam used has the same direction as the incident wave, the imaging mode is called bright-field; if it is one of the diffracted beams it is called dark-field. Both types of image will show the intensity of the selected beam, $I_g(\boldsymbol{r})(= |\phi_g(\boldsymbol{r})|^2)$, which oscillates with thickness and is also a function of the local orientation through any variations in s due to lattice distortions. These oscillations, which can have periods as small as 1 nm for moderately large values of s, can be used to obtain a three-dimensional contour map of the particle as first used by Ino (1966) and Ino and Ogawa (1967). With a very weak diffracted beam, it is possible to obtain a fairly detailed three-dimensional model of the particle (Yacaman *et al* 1980, 1983), e.g. figure 7. Local strains will change both the amplitude and period of these fringes as used to determine local strains either when particles contact (Tholen 1986) or within small particles (Marks 1985b), see figure 8. (The character of these strains appears to be very similar to what would be expected for a surface stress effect as mentioned earlier.)

A variation of this approach is to use a number of different diffracted beams, either with an appropriately shaped objective (Heinemann and Poppa 1972) or condenser aperture (Heinemann and Poppa 1970, Freeman *et al* 1977) or scan the incident angle of the electron beam in a circle (Krakow and Howland 1976). These techniques collect the full 360 degrees of scattering for a particular set of atomic planes, and are therefore more efficient in terms of detecting small particles. Some additional references on this type of technique and related techniques in a STEM instrument can be found in the book by Reimer (1984).

3.1.2. High-resolution electron microscopy. Since the commercialization of instruments with atomic scale resolution in the early 1980's, high resolution electron microscopy or HREM has become a staple tool of small particle structural research, both in terms of its ease of use and high informational content. In fact, HREM showed its promise even earlier than this in the work of Komoda (1968), who demonstrated that very small particles of gold were multiply-twinned.

Unfortunately, for these higher resolutions it is necessary to include effects from the aberrations of the microscope. These include coherent effects such as the objective lens defocus and spherical aberration, as well as incoherent effects such as fluctuations in the

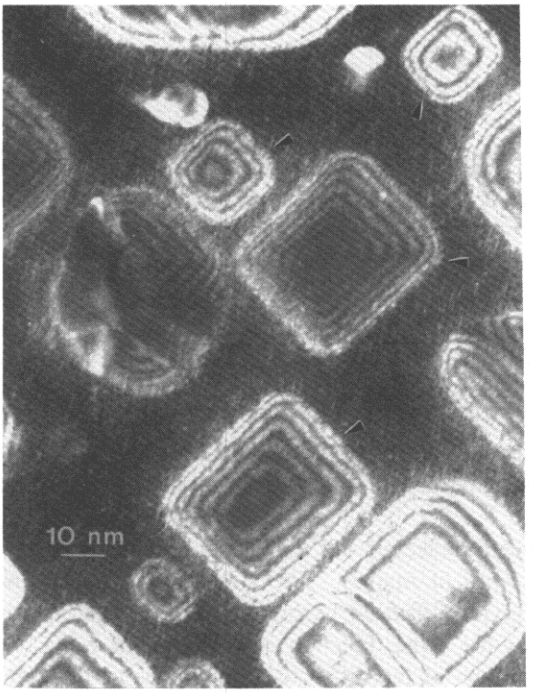

Figure 7. Weak beam image of gold particles on an amorphous carbon film (originally grown by evaporation onto NaCl). The bright fringes are equal-thickness contours, indicating that the three-dimensional particle shape of the particles arrowed is a square pyramid.

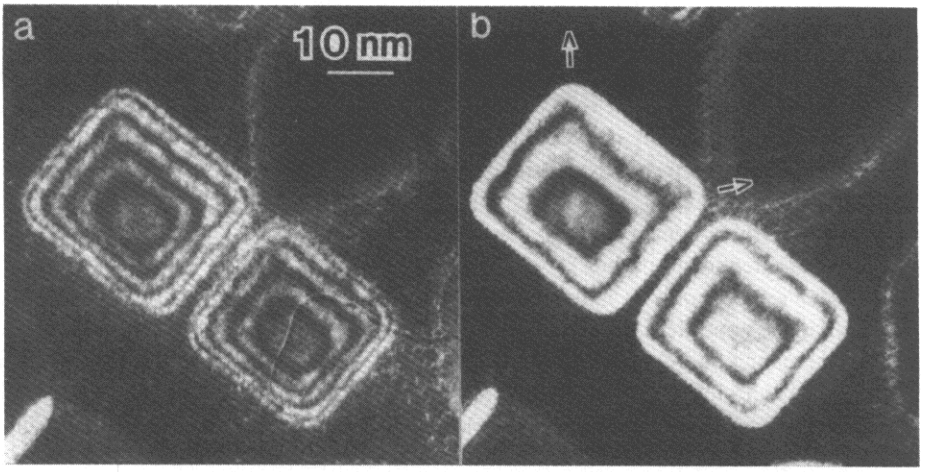

Figure 8. Dark field images of two small square pyramidal particles using two different diffracted beams in (a) and (b). The distortions in (b) indicated by the arrows correlate to inhomogeneous strains which are similar in sense to those predicted by Herring (1951). Unfortunately this is old experimental data, and as a consequence it is unclear whether the strain field is consistent with an expansion or a contraction.

electron beam voltage and direction. Provided that the amplitude $\phi_g(r)$ is changing slowly in the image plane, the image amplitude can be written as

$$I(r) = \sum_g P_g(r) \cos(2\pi g \cdot r) \tag{11}$$

where

$$P_g(r) = \sum_h \phi^*_{g-h}(r)\phi_h(r)\exp(-i\chi(h) + i\chi(|h-g|))E(h, |g-h|) \quad (12)$$

and

$$\chi(g) = \pi/\lambda(\Delta z g^2\lambda^2 + 1/2C_s\lambda^4 g^4) \quad (13)$$

with Δz the objective lens defocus, λ the electron wavelength and C_s the spherical aberration coefficient. The term $E(h, |g-h|)$ is called the envelope term, and is due to the incoherent aberrations such as energy fluctuations. For an exceedingly thin crystal where multiple scattering can be ignored so that the transmitted intensity is very large, this can be simplified to

$$I(r) = 1 + \phi_g(r)\cos(2\pi g \cdot r)[-2\sin(\chi(g))E(0, g)]\,. \quad (14)$$

This latter form is simpler to analyse, and although very commonly used in the literature is not sufficiently accurate. However, the physical picture is still representative. The image will contain fringes with spacings that represent those of the atomic planes in the solid, but the contrast and amplitude of these fringes will vary with the operational conditions of the instrument. For full rigour it is necessary to perform a numerical image simulation to confirm interpretation of the images, and examples of this can be found in the work of Flueli (1989), Buffat *et al* (1991), and Nihoul (1992). (Most practical uses of high-resolution electron microscopy only exploit its ability to resolve the local crystallographic structure in regions of a small particle. For this type of analysis image simulations are quite unnecessary.) Provided that a little care is taken, the images are quite straightforward to obtain and directly show the atomic structure in projection. A good, general reference for high-resolution electron microscopy is the second edition of the book by Spence (1988).

A typical example of experimental data is shown in figure 9. Not only is there direct atomic scale information throughout the particle, but the external surface is also well resolved. For some general examples of applications of the technique to small particles see, for instance Marks and Smith (1981), Smith and Marks (1981) and Buffat *et al* (1991).

HREM has been exploited for small particles in three ways. First, and most commonly, it is an exceedingly efficient method of obtaining local crystallographic information, and has almost completely replaced the older dark-field techniques. Secondly, it can be used in conjunction with image simulations to, determine, in principle, atomic positions to accuracies of 0.1–0.2 Angstroms (Marks 1983b, Saxton and Smith 1985). Earlier calculations were limited by computer capacity to parts of the particles, but in more recent work it has been possible to simulate essentially complete particles (Flueli 1989, Buffat *et al* 1991, Nihoul 1992). It is therefore possible, in principle, to completely determine the projected atomic positions to 0.1–0.2 Angstroms for relatively small particles, although this is at the limits of current computer storage capabilities. Finally, it can be used to obtain very high resolution information about surfaces using the so-called profile imaging technique (Marks 1983b, Marks 1986a, Smith 1986, Yagi 1988). This later approach has led to a lot of information about dynamic processes at the surface of small particles which will be discussed later.

There are two main limitations to the technique, which can sometimes be overcome by other methods. First, it only provides a projected image, and although there is some depth data this is not cleanly interpretable. Secondly, the technique images both the particles and the underlying substrate. Particularly for very small particles, it can be difficult to

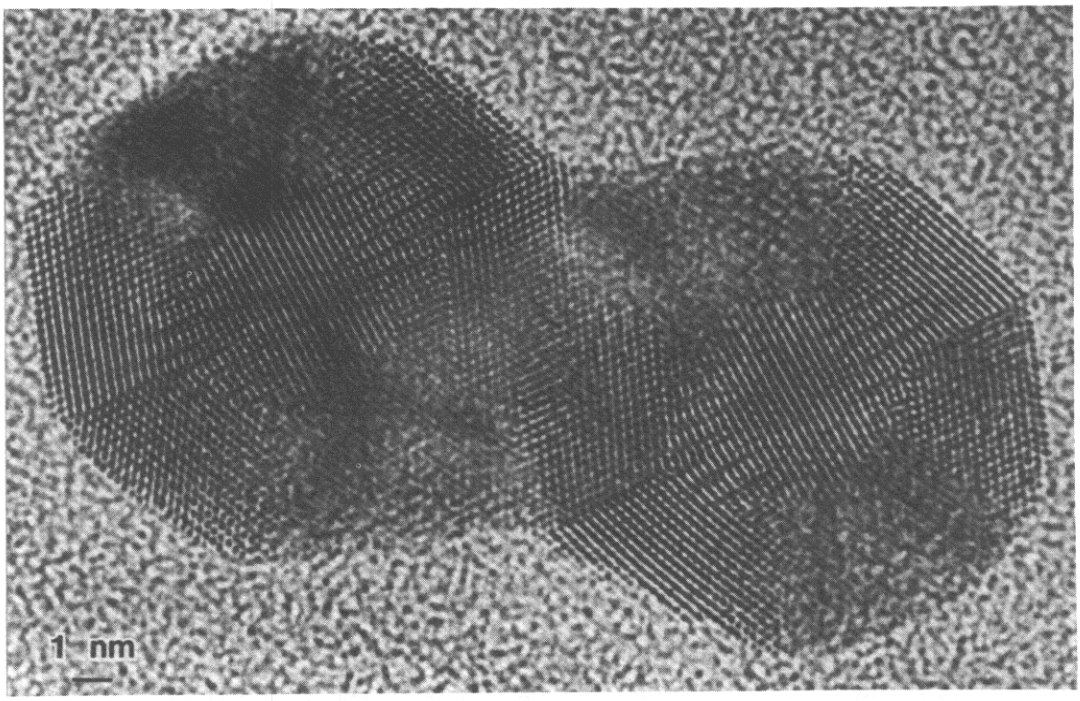

Figure 9. Typical high resolution electron micrograph of a small particle, in this case two icosahedral multiply-twinned particles which have partially coalesced together.

discriminate between the substrate structure and the particle structure (e.g. Gai *et al* 1986). A possible solution to the noise from the substrate is to eliminate this using image processing techniques (e.g. Nihoul 1992). For instance, it is possible to extract the periodic component of an image using Fourier filtering or cross-correlation averaging. (One problem is that it is possible to introduce artifacts at the same time.) Provided that the noise from the substrate is sufficiently small, it is possible to image single atoms directly as shown first by Iijima (1977), see, for instance, figure 10. It should be noted that the signal level, even for single atoms, is really quite high with modern electron microscopes, so there is no technical reason why clusters of only a few atoms cannot be imaged, a point that I will return to.

One interesting variant on the technique that has not been fully exploited to date is hollow-cone imaging (e.g. the references in the book by Reimer 1984). This approach was first developed for amorphous materials, and intrinsically has a lower 'noise' level and should therefore yield cleaner images of small particles. However, to date the technique has not been exploited in any detail, probably because the interpretation of the images is not as simple as in more conventional HREM.

3.1.3. Small probe electron microscopy techniques. A family of techniques use a rather different type of microscope, namely a scanning transmission electron microscope, where a focused electron beam of atomic dimensions is scanned in a raster fashion across the field of view. Synchronized with this raster, various different signals can be collected and displayed as images. Of particular relevance are the high-angle diffracted intensity and the plasmon-loss intensity. Using either the ratio of the diffracted to plasmon or just the diffracted intensity it is possible to obtain images where the intensity level corresponds to the integrated mass-thickness at any given point. This so-called 'Z-contrast' method

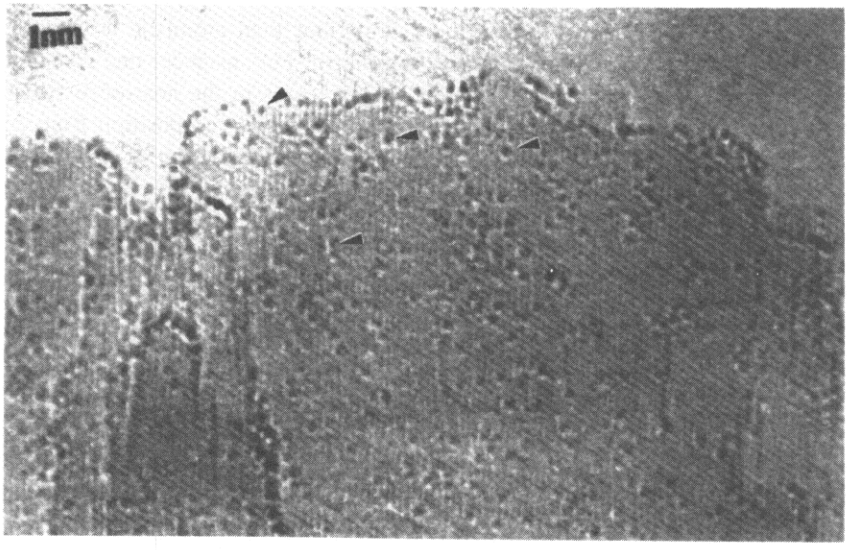

Figure 10. High resolution image showing single atoms (arrowed) on an MgO substrate.

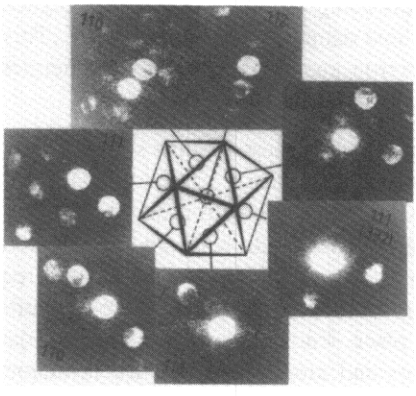

Figure 11. A collage of microdiffraction patterns taken from different regions of an icosahedral multiply-twinned particles, as indicated.

was first used by Crewe and co-workers (Crewe *et al* 1975) to image single atoms and is extensively used at the very small size regime to detect very small clusters (e.g. Crewe 1979, Treacey *et al* 1978, Pennycook 1981, Liu and Cowley 1990). There have been some recent developments where a very similar technique is used to obtain atomic images from bulk materials (e.g. Pennycook and Jesson 1991, Pennycook 1992); to date it has not been applied to small particles but it probably will be in the near future. This technique can also be used in a standard transmission electron microscope by using a conical illumination scheme as mentioned above.

It is also possible to obtain diffraction information, either with a relatively large beam (e.g. Hayashi *et al* 1976, Ohno and Yamauchi 1981, Matsumoto and Matsui 1983) or one of nanometer dimensions. With smaller probes one can obtain information from single particles e.g. (Cowley and Roy 1981, Cowley 1984), or from different segments within a single composite particle (Marks and Smith 1983a) as shown in figure 11. Much larger diffraction vectors can be collected, so it is possible to explore spacings beyond the resolution limits of HREM.

Finally, there are a large number of different techniques for obtaining chemical information; in many cases this is more important than atomistic structural information. The majority of these use the scanning approach. For instance, one can obtain chemical state information using the characteristic energy losses in the near-edge structure (e.g. the book edited by Disko *et al* 1992), measure the elemental composition from emitted x-rays (e.g. Lyman *et al* 1987, 1990) or monitor the spatial distribution of low-energy excitations (Batson 1985, Ugarte 1990, Ugarte *et al* 1992, Ouyang *et al* 1992, Batson and Heath 1993).

3.1.4. Electron damage processes. Electron microscopy is an invasive probe, and the same energy loss excitations that are exploited for small probe spectroscopies deposit energy into the sample. Although this is a significant issue, it is generally not an experimental problem. Additional details can be found in a paper by Hobbs (1979), the book by Reimer (1984) and a fairly comprehensive, critical review can be found in the PhD Thesis of Buckett (1991). There are three primary damage mechanisms:

(a) *Direct knockon damage*, where a high energy Rutherford scattering process transfers enough energy to an atom to produce vacancy/interstitial pairs or sputter an atom off the surface. The amount of energy transferred scales inversely with the mass of the target atom, and the energy transfer required to produce damage depends upon the bonding strength and the direction of the electron beam with respect to the crystal lattice. Typically light elements such as oxygen can be damaged by such a process using electrons of energies higher than 100 kV, whereas heavier elements only start to show damage about 300–400 kV. This type of process can be detected by dropping the electron energy since at lower energies any damage process will be slower or non-existent.

(b) *Radiolytic or ionization damage*, where the important process is some sort of low energy excitation such as a plasmon loss or a core-excitation in the energy range of 10–400 eV. The probability of the initial excitation scales inversely with the electron energy, so this type of effect is much stronger at lower electron energies. Although there are still uncertainties about the exact details of this damage mechanism, it is now widely accepted that it requires a relatively localized and long-lived electronic excitation in the material so that efficient transfer of electronic to nuclear motion can take place. For this reason this type of damage mechanism is not common in metallic conductors and more significant for insulators and large band-gap semiconductors. It should be noted that radiolytic damage is typically much faster than direct knockon damage.

(c) *Electron beam heating*, where all the different electron energy loss processes are transferred to thermal energy. Because this is such a simple concept, it is frequently invoked but in reality is much less significant than commonly thought. The reason is that although there are numerous calculations of the temperature rise based upon some parametrization of the energy loss processes (e.g. Gale and Hale 1961, Fisher 1970, Reimer 1984, Gryaznov *et al* 1991a), only a very small fraction of the energy deposited in a *thin sample* is thermalized; most of it escapes as x-rays or secondary electrons. This has been verified by Luzzi (1986), who has shown from direct measurements that the theoretical models substantially overestimate electron beam heating.

Although these are the three most commonly invoked damage mechanisms, they need not be the only ones. One quite significant (experimentally) effect is from the momentum transfer of the electron beam (Marks and Zhang 1992), which will tend either to line up a small particle along a primary zone axis or move it off such a zone depending upon where the particle is adhered to the substrate (the pivot point). Another interesting effect that may

be important is that in the electron beam the distribution of energies in a small particle is not Boltzmann like (i.e. not simply $\exp(-E/kT)$); due to the various energy-loss processes it will be much larger than this at high energies. It is known that the presence of such excited electronic states can lead to enhanced atomic diffusion as discussed by Borgoin and Corbett (1978).

Finally, to give a little perspective, for light elements the cross-sections for elastic and inelastic (energy-loss) processes are of the same order of magnitude. However, excepting knockon processes and momentum transfer all the energy deposition processes scale inversely with the electron energy, so far less damage is done per electron with an electron microscope than, for instance, with Auger spectroscopy. However, the electron flux at the sample may be much higher, of the order of 10^{-1}–10^{3} electrons/cm^2/second.

3.2. STM

In principle, scanning tunneling microscopy and scanning force microscopy should be exceedingly useful for very small clusters. However, to date they have not yielded extensive data. The main problems appear to be due to the tip moving clusters around (Schmidt 1993, private communication) and because the tip is relatively large compared to the small particle. What is therefore observed is some complicated convolution of the particle shape and the tip geometry, and extracting the true particle structure from this is a problem which does not appear to have been solved. For some information as to the current status see Baro *et al* (1987), Ganz *et al* (1988), Yeung and Wolf (1992), Ma *et al* (1992) and Porte *et al* (1992). We would expect that in the future these techniques may be much more powerful than they have been to date.

3.3. X-ray and electron diffraction

X-ray diffraction is a standard technique that produces some, although often relatively limited, direct structural information; for a relatively recent review see Cohen (1990). It is exceptionally powerful for small organo-metallic clusters which can be produced as single crystals, where a complete structure refinement is possible. For inhomogeneous samples it is often problematic. For instance, the line-broadening can be exploited to yield a statistical average of the particle size distribution, and in some cases this can be deconvolved to give particle size distributions. However, it should be noted that Solliard (1981) and Solliard and Borel (1988) have shown quite conclusively that this approach only works for single crystal particles. It is also possible to use the low-angle scattering regime for the same purpose; for instance Levine *et al* (1991) used this approach to track changes in both particle size and particle-to-particle separations during annealing. With larger particles it can also yield direct structural information. However, it often suffers many of the same problems as electron microscopy due to the substrate diffraction. One recently developed technique that can overcome these limitations is to exploit the rapid changes in the x-ray diffraction intensities near to an adsorption edge as shown by Georgopoulos and Cohen (1985). These authors demonstrated almost complete removal of diffraction from an alumina support material as shown in figure 12. It is not uncommon to supplement x-ray diffraction work with EXAFS studies (e.g. Sinfelt *et al* 1984); however, since EXAFS does not in general provide any morphological information about the particle as a whole it will not be discussed further here.

Electron diffraction has the advantage over x-rays (or neutrons) that the scattering cross-sections are much larger, so smaller sample volumes are required. It has the disadvantage that the diffraction theory is more complicated, and as nicely shown by Hall (1991) and

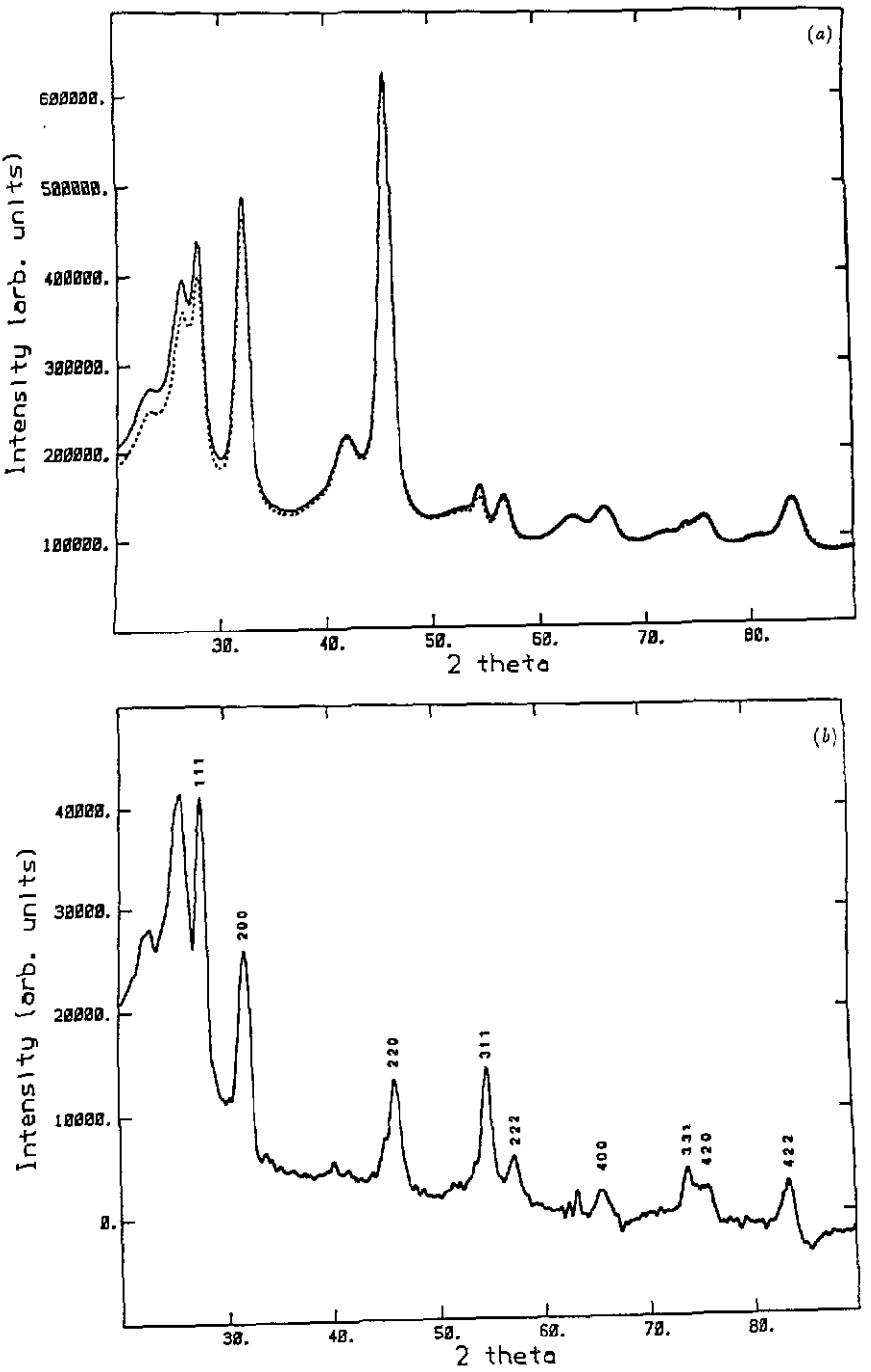

Figure 12. X-ray spectra in (*a*) obtained well below the Pt edge (full curve) and slightly below this edge (broken curve) and (*b*) by taking the difference, for particles with a mean diameter of 4 nm on alumina, courtesy of J B Cohen. It should be noted that the scattering from the particles in (*a*) is almost invisible.

Hall *et al* (1993), simple approximations can be invalid. Electron diffraction can also be combined with imaging, so many ambiguities such as the particle size distribution can be resolved directly. The most common application of electron diffraction has been to measure apparent lattice parameter changes, as mentioned previously. A second use has been to analyse particles in cluster beams. Early attempts at this (Yokozeki and Stein 1978, De Boer and Stein 1981, Kim and Stein 1982) were only partially successful; it was clear that below sizes of about 5 nm there were deviations from simple fcc structures, but the agreement between experimental and calculated diffraction patterns for more complicated structures such as multiply-twinned particles (see below) was a little inconclusive. A much more extensive analysis by Hall (1991) has been very successful. He used simulated annealing techniques to match his experimental data to particle size distributions of different morphologies, coupled with carefully calculated diffraction patterns for each morphology at different sizes. He was able to measure morphology-size distributions, conclusively demonstrating that multiply-twinned particles exist in free-floating particles.

Some comments are not inappropriate here, and these run parallel to some of the points made by Cohen (1990) in his review. The majority of analyses of x-ray diffraction data use the classic diffraction models developed many years ago (e.g. Warren 1969), and these are somewhat approximate. If one combines techniques to subtract off the substrate effects such as anomalous scattering (Georgopoulos and Cohen 1985) with the analysis methods of Hall (1991), far more information should be extractable. Given the availability of synchrotron sources and high-speed computers this should not be difficult.

4. Static structures of larger particles

It is rather common to find more than one structure in a population of small particles, and for any particular structure more than one epitaxy with respect to the substrate. A typical example of a field of view is shown in figure 13 for silver particles grown in UHV on NaCl substrate, where approximately 60% of the particles are equally divided between single crystals and two types of multiply-twinned particles, and the remaining 40% are more complicated structures. In this section I will review much of the experimental information about these various different types of particles.

4.1. Single crystals

For many materials moderate sized particles, i.e. several hundreds of Angstroms in size, are simple single crystals, without any complications. In this case the equilibrium structure is a Wulff construction for a free-floating particle or a Winterbottom (1967) construction when the substrate adhesion is important. The most commonly reported structure at small sizes is a truncated octahedron combining (111) and (100) facets as illustrated in figure 14 (see Sundquist 1964, Hayashi *et al* 1977, Fukaya *et al* 1978, Yacaman and Dominguez 1980, Yacaman *et al* 1981m Dominguez *et al* 1982, Drechsler 1985, Flueli and Borel 1988m Bonevich 1989). Larger particles, as reported by a number of authors (Flytzani-Stephanopoulos *et al* 1977, Heyraud and Metois 1980a, b) appear to be more rounded. It is not clear whether this is a finite size effect as mentioned earlier, or due to differences in the cleanliness or conditions of the experiments. Only for the larger particles was tight control of the surface conditions achieved, but there is also the possibility that the small particles, since they are able to equilibrate much faster than larger ones, represent lower temperature equilibrium shapes. It is appropriate to mention data by Wang *et al* (1985) for small Pt particles and Henry *et al* (1991), both of which show very large changes in

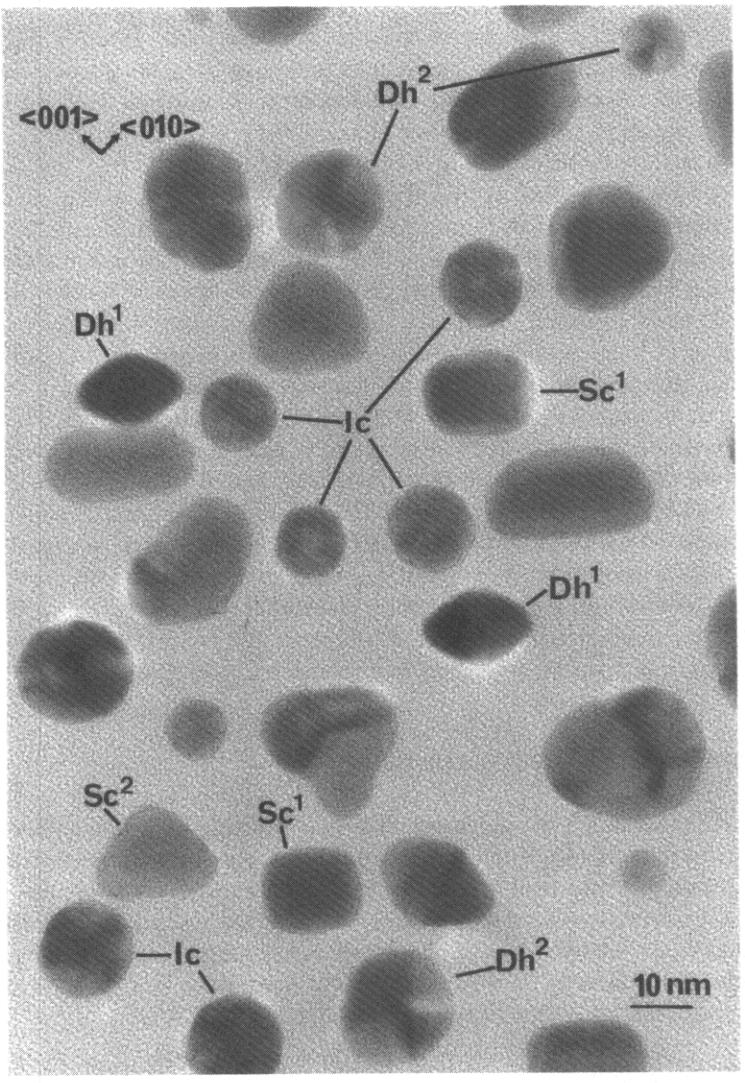

Figure 13. Field of view of silver particles grown epitaxially on NaCl. The different particle types indicated are: icosahedral MTPs (Ic); Decahedral MTPs with ⟨100⟩ and ⟨111⟩ epitaxies (Dh^1 and Dh^2), and single crystals with ⟨100⟩ and ⟨111⟩ epitaxies (S^1 and S^2). The orientation of the substrate is indicated.

the shape of particles depending upon the preparation conditions. For instance, Wang *et al* (1985) show a dramatic change from somewhat cubic particles to essentially spherical ones after annealing in different gases.

In many cases the experimental structure is not the Wulff shape, but clearly determined in large part by growth kinetics. Particles with a (111) epitaxy often have a triangular external profile with a tetrahedral shape, whereas with (001) orientations the most common habit is square pyramidal as shown previously in figure 8.

A very large collection of data is also available for most of the pure elements from inert-gas experiments, e.g. Yatsuya *et al* 1973, Kasukabe *et al* 1974, Uyeda 1974, Ohno *et al* 1976, Hayashi *et al* 1977, Ohno and Yamauchi 1981, Matsumoto *et al* 1983. In general

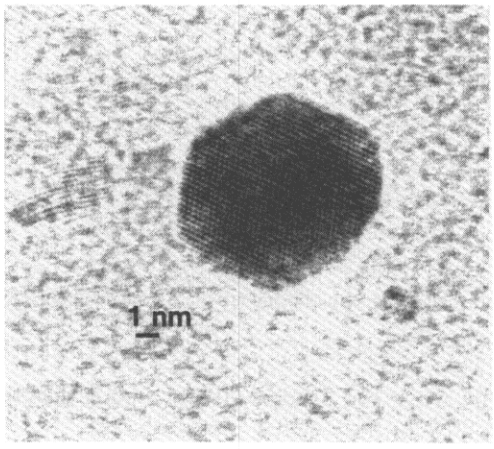

Figure 14. High resolution image showing a small single crystal particle of gold which is roughly a Wulff construction shape with (111) and (100) facets.

these particles are very similar to the Wulff construction shapes, although it is not clear in every case whether these are the equilibrium shapes or kinetic shapes, since the growth mode is strongly kinetic. A detailed discussion of some of the more recent Japanese work in this area can be found in the paper by Uyeda (1991).

4.2. Single crystals with twins or stacking faults

Quite often single crystals are combined with particles containing simple twins or stacking faults. These are thought to occur either by growth mistakes, by coalescence of multi-positioned particles during epitaxial growth or due to internal strains caused, for instance, by a martensitic transformation (Tholen 1981). In some cases a family of parallel twins is formed, leading to what is called lamellar-twinned particles or LTPs. The largest data base for this type of particles is from the inert-gas work mentioned above.

The experimental structures match fairly well the predictions of the modified-Wulff construction (Marks 1983a). In some cases rather asymmetric twinned structures are also observed, and these can also be explained within the same model. Atomistic calculations by Farges *et al* (1989) and Cleveland and Landman (1991) also indicate that symmetric twins are comparatively stable structures, although they did not explore asymmetric ones. It should be noted that although the experimental structure of these particles is qualitatively consistent with these theoretical models, they have not been tested to the same degree as those of single crystals or multiply-twinned particles (see below).

4.3. Multiply twinned particles

Although small particles are often single crystals, a common exception is what are called multiply-twinned particles or MTPs. First discovered almost simultaneously by Ino (1966), Ino and Ogawa (1967) and Allpress and Sanders (1967), they have since been studied extensively, far more so than simpler single crystals. (For completeness, there are even earlier references to five-fold particles, for instance the work of Melmed and Hayward in 1959.) A recent review (Ajayan and Marks 1990) includes a fairly extensive coverage of their observations in different materials. One quite recent development has been the observation of these structures in small diamond particles (e.g. Matsumoto and Matsui 1983, Narayan *et al* 1989), and millimeter sized fullerene crystals (Haluska *et al* 1993). It should be noted that the presence or absence of MTPs depends strongly upon how the

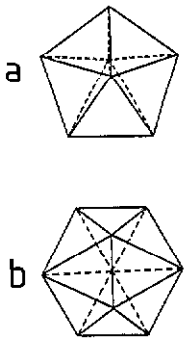

Figure 15. Schematic diagram of a decahedral MTP in (*a*) and an icosahedral MTP in (*b*).

small particles are prepared as first noted by Avery and Sanders (1970), a point that will be returned to below.

Ino's original approach to modelling these particles was in terms of arrangements of twin-related tetrahedra packed along (111) faces. Five such units can be arranged to form a pentagonal bipyramid, twenty an icosahedron as illustrated in figure 15. Particularly for the five- fold particles the pentagonal bipyramid is not general enough, and it is better to consider them in terms of their symmetry groups. I will use the notation of describing the five-fold particles of the D_{5h} symmetry group as decahedral MTPs; the icosahedral particles which belong to I_c as icosahedral MTPs. The single crystal assemblies are not fully space filling, so some form of inhomogeneous strain or distortions of the bond lengths is required to produce a space-filling structure. The distortion required for a decahedral particle is relatively simple, and corresponds to a simple angular gap or wedge Volterra disclination of about 7.5 degrees. The distortion for an icosahedral particle is a little harder to visualize, and corresponds to six such disclinations running through the particle along the directions joining the apexes of an icosahedron to the centre.

When MTPs were originally discovered, there was substantial debate as to their growth mechanism. Four primary models have appeared in the literature. The first was that they are due to errors during the growth leading to twins (Allpress and Sanders 1967). The second was that they were intrinsic equilibrium structures of lower energy at smaller sizes (Fukano and Wayman 1969, Ino 1969). The third model is that they are associated with a phase transformation to an orthorhombic or rhombic form (Bagley 1965, Yang 1979, Schabes-Retchkiman *et al* 1982, 1984). The last model was that they grew by layer growth around the five-fold symmetry axes, and were thus kinetic phenomena (Gillet 1977). The vast majority of the evidence now clearly favors an intrinsic equilibrium structure. The most convincing experimental evidence is the work of Yagi *et al* (1975) who directly observed transformations to MTPs both during growth and particle coalescence, data which is almost impossible to explain on any other basis. More recent observations of structural fluctuations between different particle morphologies *in situ* within electron microscopes (Iijima and Ichihashi 1986, Smith *et al* 1986) can also not be explained by any kinetic or twinning model.

There is very little experimental refinement of the external shape of the icosahedral structure in the literature, although as can be seen from the careful analysis of Buffat *et al* (1991) the external surface is rarely as sharp as that of a perfect icosahedron. For the decahedral particles, a variety of different morphologies have been observed. A common observation is a relatively perfect pentagonal bi-pyramid structure, see for instance figure 16. A quite different structure was first reported by Marks (1984) for annealed particles with re-entrant surfaces at the twin boundaries as shown in figure 17. Although at first sight this appears to be a strange shape, it is the minimum energy configuration that is predicted by

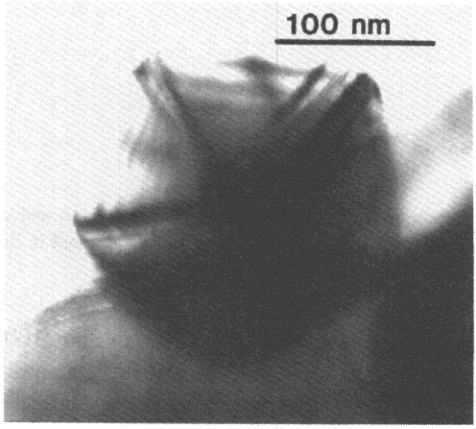

Figure 16. Image of a rather large decahedral MTP which is an almost perfect pentagonal bipyramid, taken from Marks and Howie (1979).

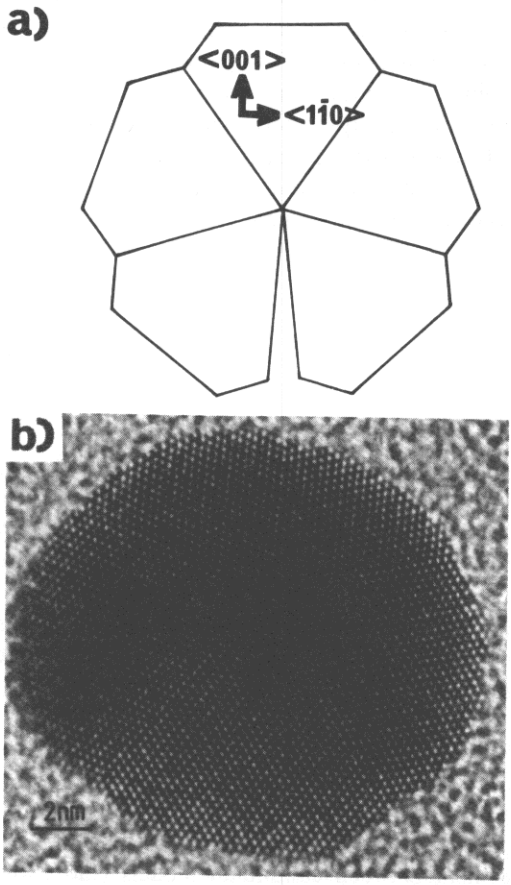

Figure 17. Calculated Modified Wulff construction shape in (*a*) and experimental data in (*b*). The re-entrant surfaces at the twin boundaries and the much more rounded shape compared to that in figure 16 should be noted.

the modified Wulff construction, see figure 17. Subsequent to this there have been numerous other observations of the same structure. As mentioned previously, the re-entrant surfaces will be highly favorable growth sites, and should not appear under kinetic conditions such as those employed in the early work (Ino 1966, Ino and Ogawa 1967 and Allpress and Sanders 1967). At small sizes the decahedral particles typically have only (111) and (100) facets. Somewhat larger particles can have additional facets leading to more rounded shapes (Marks 1984) and in some cases very rounded particles have been observed. It should be

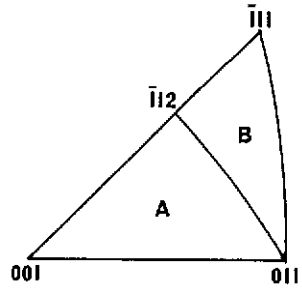

Figure 18. Stereographic triangle subdivided into two regions *A* and *B* which play a role in the total surface energies of MTPs as described in the text.

appreciated that there is really no reason for these particles to only have (111) and (100) facets; the external shape of any one segment is the same as that of the appropriate single crystal shape in the region bounded by two or three (111) planes for the decahedral and icosahedral particles respectively.

The first detailed analysis of the energies of MTPs relative to single crystals was performed by Ino (1969) using a continuum based model with homogeneous strains. This was later extended by Marks (1984) and Howie and Marks (1984) who improved both upon the model for the external shape and the strain field. Within this model the fundamental reason why MTPs form is that they contain more low energy facets than single crystals, in particular more (111) and less (001). The change in exposed surfaces can be quite well represented using a stereographic triangle as illustrated in figure 18, subdivided into two sections A and B (Marks 1984). The two types of MTPs and single crystals have surfaces corresponding to

$$\begin{aligned} &\text{(a) Single crystal} = 48A + 48B \\ &\text{(b) Decahedral MTP} = 40A + 60B \\ &\text{(c) Icosahedral MTP} = 120B. \end{aligned} \tag{15}$$

Taking into account the relative areas it can be shown that MTPs may be of lower energy if the mean surface free energy of domain A is more than 0.963 times the mean surface free energy of domain B. Whether they are of lower energy will depend upon an energy balance between a gain in total surface free energy and the strain energy required to close the particles.

These surface energy changes, and the internal strain energy needed to close the particles can be easily expressed in a continuum model. Following Howie and Marks (1984), the total free energy can be expanded in the form

$$G = [\xi_w + \xi_{ss}]\gamma_{111}V^{2/3} + \xi_s V \tag{16}$$

where ξ_w parametrizes the surface free energy, ξ_{ss} that due to the surface stress (see below) and ξ_s is the energy required to distort the particles elastically.

There is starting to be quite good agreement between continuum models (Ino 1969; Marks 1984, Howie and Marks 1984) and atomistic ones (Farges *et al* 1980, Cleveland and Landman 1991, Uppenbrink and Wales 1992) concerning both the external shape and the strain energy terms. In a continuum model the surface morphology can be found using the modified Wulff construction as discussed earlier. For the icosahedral particle, the shape that has been used in most theoretical analyses is a perfect icosahedron. Farges *et al* (1980) mention that minor improvements can sometimes be obtained by eliminating the five-fold apex atoms, and similar conclusions were found by Marks (1984) although this feature

was not found in the calculations of Cleveland and Landman (1991), presumably because a different potential was used. For the decahedral particles the re-entrant shape mentioned above in figure 17 is the lowest energy configuration from both the continuum analysis of Marks (1984) and the atomistic ones of Raoult *et al* (1989) and Cleveland and Landman (1991). (A slightly different form for the surface was used by Ino (1969) which does not include re-entrant surfaces at the twin boundaries. Without these re-entrant surfaces, it is not possible to explain the stability of the decahedral particles.)

The elastic strain energy can be calculated based upon models that involve homogeneous strain (Ino 1969) or disclinations (DeWit 1972, Howie and Marks 1984, Dundurs *et al* 1988, Polonsky *et al* 1991). The simplest case is the decahedral particles, for which the displacement field was first presented by DeWit (1972), and takes the form

$$u_r = \epsilon_d[(1-2\nu)/(2(1-\nu)r\ln(r/R) - r/2] \tag{17}$$

$$u_\theta = r\epsilon_d \tag{18}$$

where u_r and u_θ are the radial and angular displacements, ϵ_d is the angular deficit in the particles (0.0205) and ν Poissons ratio, leading to a total strain energy (per unit volume) of

$$\xi_s = \mu\epsilon_d^2/4(1-\nu) \tag{19}$$

where μ is the shear modulus. A more complete solution using a three-dimensional sphere has been presented by Polonsky *et al* (1991), and leads to a result which is about 10% smaller than this and, importantly, has the same dependence on the particle size (i.e. the total stored strain energy is proportional to the particle volume).

The original solution for the icosahedral particles by Howie and Marks (1984) used an approach developed by Yoffe (1980) distributing the angular gap homogeneously throughout the particle. This gives a very similar result, with a strain energy density of

$$\xi_s = 2\mu\epsilon_d^2(1+\nu)/(1-\nu)\,. \tag{20}$$

This is approximately ten times that of the decahedral particles. In principle a better solution could be obtained as noted by Polonsky *et al* (1991) by superimposing six disclinations within an elastic sphere, but to date this result does not appear to have been published. For both types of particles there is a compression in the centre, and an expansion at the outer surface.

An important additional term that needs to be considered is the change in surface free energy due to the elastic strain field, i.e. the surface stress contribution (Howie and Marks 1984). This term is comparable in magnitude to the differences between the energies of different particles, and more than an order of magnitude larger than the twin boundary terms which are negligibly small. Unfortunately, obtaining an accurate estimate of this term is exceedingly difficult, particularly for complicated morphologies. The approach adopted by Howie and Marks (1984) was to include the surface geometry using the term ξ_w, i.e. to write

$$\xi_{ss} = \langle\sigma\rangle\langle e\rangle\xi_w \tag{21}$$

where $\langle\sigma\rangle$ is a mean surface stress and $\langle e\rangle$ the mean strain in the surface.

The general conclusion is that the icosahedral particles may be stable at very small sizes, then the decahedral particles and finally single crystals at large sizes. This is the

case both in the continuum model and the atomistic calculations of Farges *et al* (1980) and Cleveland and Landman 1991. Importantly, the model showed that this ordering was very sensitive to the surface free energy and surface stress terms; this builds in a dependence of experimental particle structures upon the cleanliness of their surfaces, the preparation temperature as well as variations from material to material. A similar dependence upon the form of the atomic potential used has been demonstrated by Uppenbrink and Wales (1992), although unfortunately these authors used the wrong shape for the decahedral particles. One of the confusing aspects of research in this area is conflicting results as to the presence or absence of MTPs for the same material; this can be immediately understood as changes in the stability due to surface impurities. However, the comments made in the introduction about how far one can use this type of energy ordering to explain experimental results merit repeating; it is only under very special circumstances that one can make any type of connection between the relative energies of different particles and experimental data.

Although the *mean* distortion in the particles is equivalent to models based around orthorhombic or rhombic symmetry (Bagley 1965, Yang 1979, Schabes-Retchkiman *et al* 1982, 1984), the case for inhomogeneous strains in these particles appears to be very strong. There is strong evidence for such strains in dark-field images (Marks 1985b), diffraction patterns from single segments (Marks and Smith 1983a) and the inhomogeneous model (Howie and Marks 1984) is in quite good agreement with the strain relief mechanisms in larger icosahedral particles (Marks and Smith 1983a), see for instance figure 19. There is also some evidence for stress relief in small decahedral particles involving a splitting of the disclination, as discussed by Gryaznov *et al* (1991b), who also show qualitative agreement with experimental results by Marks and Smith (1983a), Iijima (1987) and Giorgio and Urban (1988). There is also quite good experimental evidence for converting the inhomogeneous strain into a low-angle grain boundary in larger particles as first noted by Fukano and Wayman (1969), as shown in figure 20. (A full, systematic analysis of experimental stress relief mechanisms in decahedral particles appears to be a good topic for further work.) Atomistic calculations (Farges *et al* 1982, Raoult *et al* 1989, Cleveland and Landman 1991) also show inhomogeneous strains which are quite compressive at the centre.

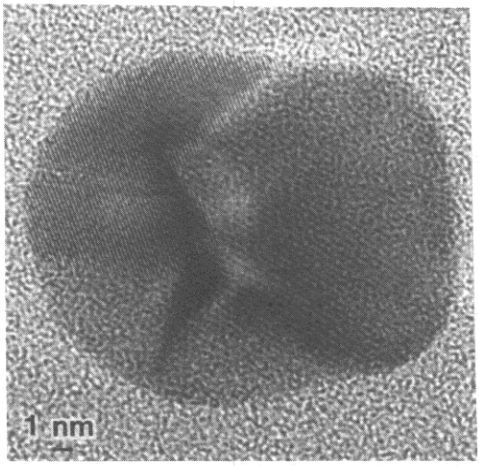

Figure 19. Experimental image of strain relief in an icosahedral MTP through a dislocation as arrowed.

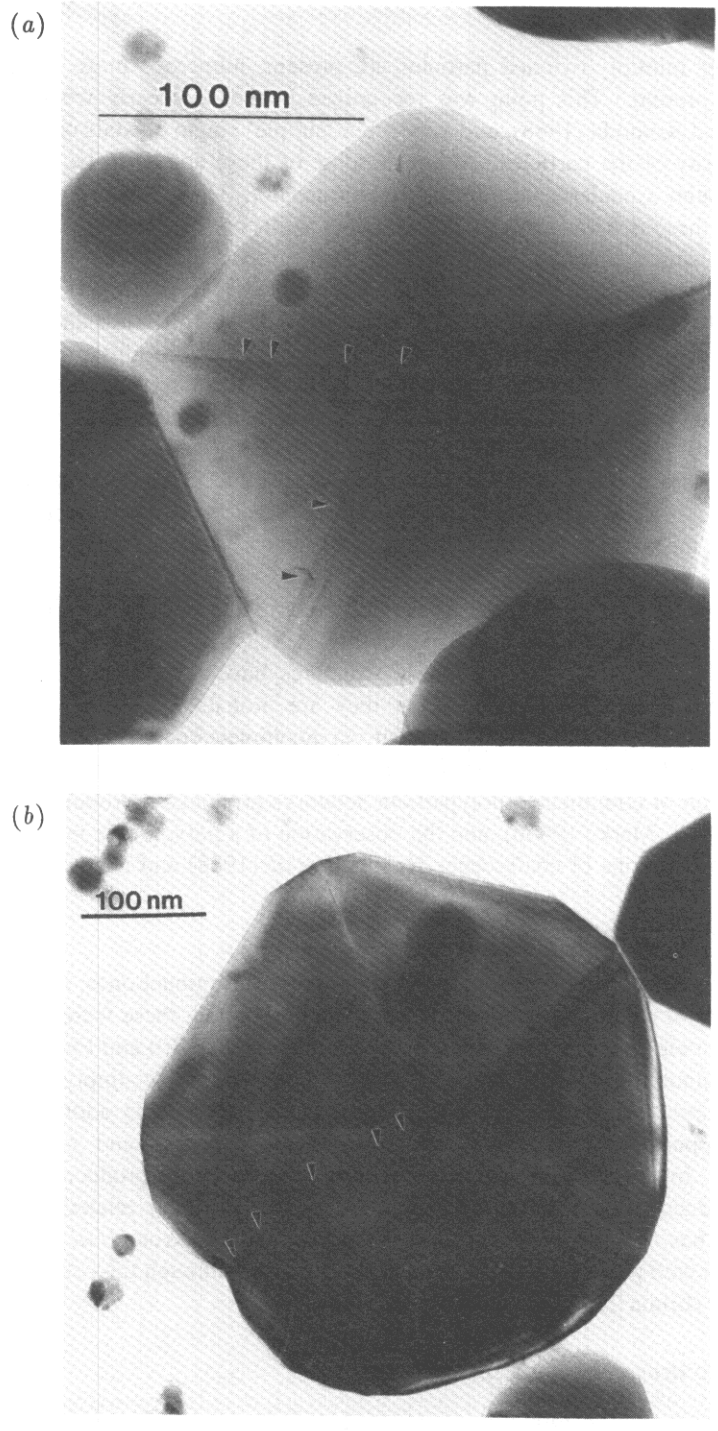

Figure 20. Stress relief to produce low angle grain boundaries in large decahedral MTPs in (*a*) from a silver particle where the dislocations (arrowed) are at two of the twin boundaries, and in (*b*) from Ge where the dislocations (arrowed) are in the middle of a single segment, courtesy of N Tanaka.

4.4. Polyparticles

Whenever multiply-twinned particles are present, numerous more complicated structures are also present. This point was recognized in the very early work by Ino and Ogawa (1967) and Komoda (1968), and very often 'simple' single crystals or MTPs do not represent the majority of the particles. Although some of these appear to be structures trapped part way through a coalescence process, many are not. One model which appears to explain many of these is a variation on the modified-Wulff construction used for MTPs as discussed earlier. Using the same idea of dividing the segments along twin-boundaries it is possible to produce numerous more complicated structures (Marks 1983a). Many of the shapes predicted by this model are in fact found experimentally (Smith and Marks 1981). There are also direct analogues of these in small organometallic clusters; for instance, the ion $[(Ph_3P)_{12}Au_{13}Ag_12Cl_6]^{m+}$ consists of two Au-centred Au_7Ag_6 icosahedra sharing a common Au vertex (Teo and Keating 1984) and other more complicated poly-icosahedral structures (Teo *et al* 1990). Significantly, the total surface free energies of the more complicated structures are not dissimilar to those of simpler MTPs, a point of relevance later when we consider non-static structures. Similar to the situation with respect to lamellar twinned particles, the experimental structure of this class of particles has not been explored very deeply.

The exact origins of some of the more complicated forms of these particles is not a completely resolved issue. One possibility is that they grow from small polytetrahedral nuclei. However, the fact that these structures have not been reported during structural fluctuations (see below) implies that they are probably not very stable structures. An alternate kinetic model is that they occur via incomplete coalescence of particles as proposed by Smith and Marks (1981). There appears to be some evidence to support this based upon observation of complicated polyparticle networks produced by room temperature growth of gold on KCl (Marks 1986b), and the observation of a polyparticle intermediary by dynamic HREM observations of coalescence by Flueli *et al* (1988) and Miki-Yoshida *et al* (1992).

4.5. Other morphologies

Although the structures detailed above are often the dominant ones, it would be exceedingly misleading if the reader was left with the impression that these were the only ones. One of the largest classes, as noted both by the author (Marks 1980) and Flueli (1989) is structures which cannot be readily identified. In many cases these may simply be particles which are not appropriately oriented for imaging, but there are certainly additional structures which do not appear to correspond to any of the current models, and an example is shown in figure 21. In some cases more extreme morphologies can be produced due to kinetic factors as mentioned previously. One relatively unique structure, related to the MTPs in many respects, has recently been observed in carbon-clusters (Kroto *et al* 1985). These are cage structures with predominantly icosahedral structures, although tube-structures have also been observed (Iijima 1991, Ebbesen and Ajayan 1992).

4.6. Static structure of very small clusters

There are many uncertainties concerning the structure of clusters in the few tens of Angstroms size scale due to lack of experimental data. Some liganded clusters which can produce single crystals are the only noticeable exception to this. The vast majority of the work has been theoretical, and the results often depend upon the choice of model; it is rarely possible to perform full *ab initio* calculations except for very small clusters. Some

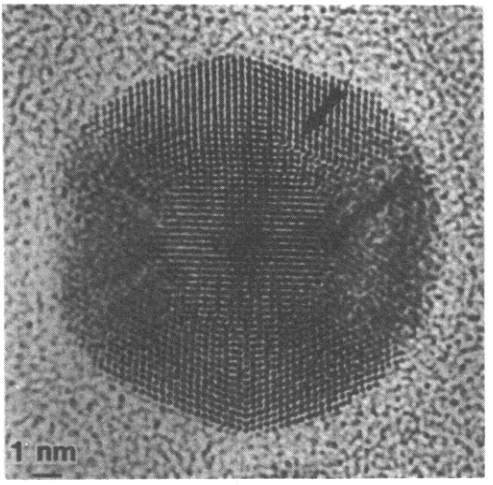

Figure 21. High resolution image of a quite distorted decahedral MTP which does not appear to fall into any simple classification.

recent reviews of theoretical work for clusters up to about ten atoms can be found in the work of Koutecky and Fantucci (1986) and Bonacic-Koutecky *et al* (1991).

The earliest and seminal work was performed by Hoare and Pal (1971, 1972, 1975). Using simple Leonard–Jones potentials, these authors demonstrated that very small clusters could have more complicated structures; in fact they observed multiply-twinned structures. Here I will not attempt to review the more recent literature, which is vast; a number of recent papers can be found in a recent conference proceedings edited by Berry *et al* (1993). The literature seems to be fairly consistent in that very small clusters in the size range 4–100 atoms are often quite complicated, not simply single crystals but often complicated polyhedral conformations.

5. Non-static structures

Excepting the work of Hoare and Pal (1971, 1972, 1975) and Yagi *et al* (1975), almost all of the early research focussed on static structures. The theoretical questions which were being asked were the lowest energy structures, and the experimentalists were attempting to determine these. However, with improvements in computers and numerical techniques as well as electron microscopy techniques, dynamics has become a recent issue. Not only has this led to new results, it has also raised questions about how structures in small particles should be considered.

5.1. Fluctuating structures in smaller particles

It is now fairly well established, both from computer simulations and from experimental data on small organo-metallic cluster, that small clusters do not always have a structure at realistic temperatures, but instead are fluctuating (undergoing isomeric conversions) and do not have a sharp melting temperature. Many of the key points seem to have appeared in separate literature sources independently, and I will attempt to summarize some of the key points here; a selection of relevant theoretical papers is the work by Berry *et al* (1984), Jellinek *et al* (1986), Sawada and Sugano (1989, 1991), Wales and Berry (1990a, b), Berry (1990), Bernholc *et al* (1991), Matsuoka *et al* (1992), Valkealahti and Manninen (1992), Vlachos *et al* (1992a, b)

A good starting point is the analysis of Hoare and Pal mentioned earlier. Their calculations indicated that the energy barriers between different structures were somewhat small and could easily be overcome at relatively low temperatures. One specific example of an interconversion mechanism is the transition from icosahedral to cubo-octahedral. As mentioned by a number of authors (Mackay 1962, Farges *et al* 1980, Marks 1980, Wallenberg 1987) this can occur through a vibration of the cluster as a whole, and this has been observed in calculations by Valkealahti and Manninen (1992). This mechanism has been proposed to explain the temperature dependence of the carbon NMR of $Fe_3(CO)_{12}$. The structure of this complex is very close to an icosahedral arrangement of carbonyls about an iron triangle. At low temperatures (<178 K), ^{13}C NMR and x-ray data indicates an icosahedral structure. However, as the temperature rises the NMR data changes, indicating that rapid exchange of the carbonyls is taking place as discussed, for instance, by Johnson and Rodgers (1990). There is also some evidence for metal atom rearrangements in even larger clusters, for instance $Rh_{55}[P(tert-Bu)_3]_{12}$ where ^{103}Rh NMR suggested rapid exchange of the Rh atoms (Schmid *et al* 1984), although the evidence here is not so conclusive.

A number of authors have performed molecular dynamic calculations and observed both structural transformations and coexistence between solid and liquid states as discussed originally by Berry *et al* (1984). Whereas a coexistence regime appears to be fairly well established, the data on structural fluctuations is a little limited particularly since many of the calculations are for very small (<13 atoms) clusters. Two particular analyses for slightly larger clusters by Sawada and Sugano (1989) and Matsuoka *et al* (1992) seem to offer reasonable evidence, and in a later paper Sawada and Sugano (1991) try to make a direct comparison between their data and electron microscope data (see below). Unfortunately it is very difficult to make this connection since the time scales for the calculations are quite short, and the cluster sizes rather small.

Is there any experimental evidence for this type of structural fluctuation from electron microscopy? There is, in fact, exceedingly strong evidence that this is the case. It was shown many years ago by Iijima (1977) that imaging single atoms by high resolution electron microscopy is not difficult. If the structures are static, they should have been successfully imaged. As far as I am aware, there is not a single experimental HREM image which clearly resolves the atomic structure of clusters of a few atoms. By induction, the clusters have to be fluctuating (under the conditions of the experiments), and there is experimental evidence for this in some of the original data by Crewe (1979) and also some more recent data by Mitome *et al* (1989).

5.2. Fluctuating structures in larger particles

Although single crystals are probably the most common particle habit observed experimentally, multiply-twinned particles and many more complicated structures are very common in fcc metals such as silver and gold as discussed above. Such data hints that simple ideas of a single equilibrium structure which all particles of a given size adopt may not be completely correct even for these larger particles. One compelling piece of early experimental data is the transformations between different particles observed experimentally by Yagi *et al* (1975). There is also some data supporting dynamic structural changes in clusters of only a few atoms from early STEM work (Crewe 1979). Around the middle of the 1980's some new results appeared which reinforce these conclusions. Two groups (Iijima and Ichihashi 1986, Smith *et al* 1986) independently observed structural fluctuations between different structures in high resolution electron microscopes. An example of the phenomenon is shown in figure 22.

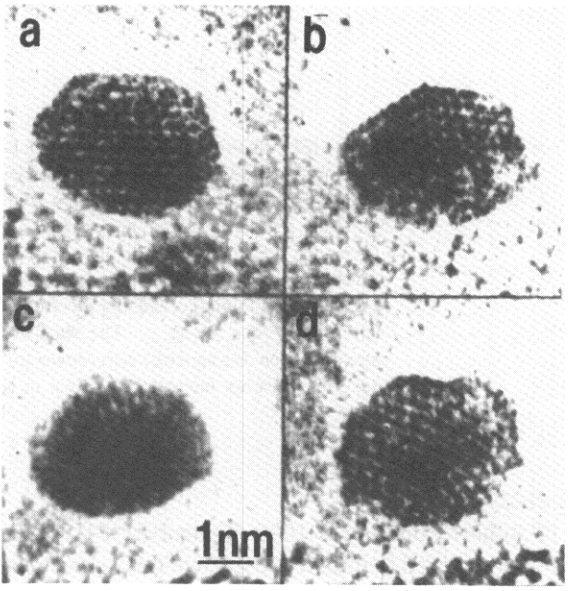

Figure 22. Sequence of particle shapes during electron microscope observation, curtesy of D Narayanaswamy: (*a*) single crystal; (*b*) single twin; (*c*) icosahedral MTP and (*d*) decahedral MTP.

It is appropriate here to briefly summarize some of the experimental observations of this phenomena, which I will refer to as 'quasi-melting'. It seems to be fairly common to many different materials, primarily the fcc metals, although in some cases there are complications due to electron-beam induced reactions in the microscope. The observation is that a single particle on the time scale of seconds will change, in an apparently random fashion, between being a single crystal, a lamellar twin, a decahedral MTP or an icosahedral structure. Not only symmetrical forms of these particles are observed, but also many asymmetrical twins. (To date there are no reports of more exotic structures such as polyparticles during these transformations.) The transition from one shape to another is faster than available recording techniques (TV cameras and videotape) and the particles reside in one given structure for some time (seconds to minutes).

Several models were proposed to explain these results, and they can be grouped into two classes. The first class was that some relatively violent process was taking place such as a Coulomb explosion (Howie 1986), an Auger cascade (Williams 1987) or charging (Iijima and Ichihashi 1986). (It should be noted that there is independent evidence from XPS spectra (Wertheim 1990) for transient charging effects in small particles.) In all of these the general idea is that the particle effectively melts and then recrystallizes in a different structure. A related model that is often quoted is that the whole process is simply due to electron beam heating of the sample (Smith *et al* 1986; Mitome *et al* 1989), and that transitions are taking place in particles which are very close to their melting point. The second approach goes back to some of the ideas mentioned above and questions whether there is a true thermodynamic lowest energy structure that every particle adopts, or a population of structures statistically occupied.

At present the evidence appears not to be consistent with any of the violent models or with electron beam heating as the *dominant* effect. To summarize the data:

(a) Calculations of electron beam heating (Dundurs *et al* 1988, Gryaznov *et al* 1991a) and experimental measurements of the energy losses (Rez and Glaisher 1991) do not support ideas of a temperature very close to either the melting point of the bulk material or the depressed melting point of a small particle. (Theoretical models lend tooverestimating

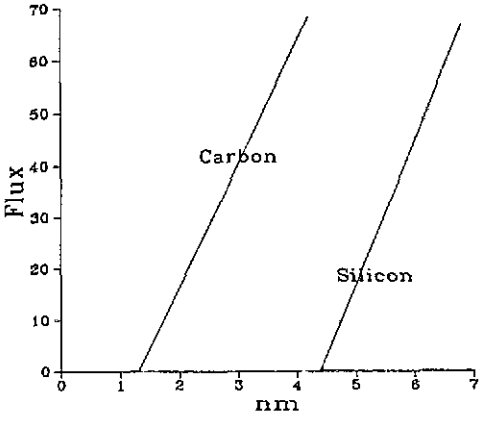

Figure 23. Replotting of the results of Lewis and Smith (1989) for small gold particles on either graphitic or amorphous carbon (the two data sets overlap) and on amorphous silicon. Above the lines drawn the particles fluctuate in structure, below it they do not, with axes of the particle radius along x and the electron beam flux in amps/cm^2 along y. The experimental data has been extrapolated here down to zero flux, and does not intercept the origin in either case.

electron beam heating effects, as discussed earlier.)

(b) It has been reported by a number of authors (Smith *et al* 1986, Wallenberg 1987, Ajayan and Marks 1989b) that the electron flux required to initiate the fluctuations is much larger than that to sustain them. In fact the process does not stop when the electron beam is reduced or even turned off for a short period (Ajayan and Marks 1989b).

(c) Measurements of the particle size versus electron flux dependence by Lewis and Smith (1989) (see figure 23) do not extrapolate to zero fluctuations in the absence of the electron beam.

(d) Both silver and lead undergo structural fluctuations (Malm 1991, Malm *et al* 1991, Bovin and Malm 1991, Narayanaswamy 1993). Since silver has a relatively high vapour pressure near its melting point and lead a very low melting temperature, these place severe restrictions on the temperature of the experiments

What does appear to be critical is that there is a relatively weak adhesion of the particles to the substrate (Smith *et al* 1986, Wallenberg 1987, Ajayan and Marks 1989b) as quite nicely shown by Giorgio *et al* (1991a, b). A quite telling piece of experimental data has been presented recently by Lin *et al* (1993). These authors observed changes in the field emission from single clusters as a function of time which they attribute to structural fluctuations. Since there is no high-energy electron beam in these experiments, it is almost impossible to explain this data except by dealing with the structural fluctuations as an intrinsic effect.

An alternative model considers that the morphology of a small particle is best represented by a potential energy surface. This concept is (reading between the lines) present in the early work of Hoare and Pal and also appears in the work on organometallic clusters mentioned above. In this case the 'structure' of a small particle is not necessarily the lowest-energy configuration, but is instead controlled by the shape of this surface, particularly the depth of local and global minima.

One of the more important aspects of this model is how it influences thinking about small particle structures. As mentioned earlier, much of the analysis, both theoretical and experimental, has focussed upon the idea of a single lowest-energy structure. Conventional thermodynamics tells us that if we observe a population of small particles, or one single particle for 'long enough', what will be found is a Boltzmann-like distribution of structures as a function of their energy. Unfortunately thermodynamics is of no help in telling us how long we have to look at a single particle, years or seconds; this is the realm of kinetics.

The interpretation of the experimental observations of the structural fluctuations is that, for *whatever reason, the appropriate time scale is seconds.*

The basis of this model has been reviewed recently (Ajayan and Marks 1990, Marks and Doraiswamy 1994) and only the key elements will be detailed here. Explicit calculations for part of the potential energy surface corresponding to changes in the structure of a decahedral particle showed that the barriers between local minima were relatively small, and could be overcome with a relatively small thermal fluctuation. Based upon this model one can calculate a temperature at which the thermal fluctuations will be large enough to overcome the potential energy barriers and there is a 'phase transition' to a state (phase) which we have called a 'quasi- molten' state where the particles are constantly changing shape. The reason behind this nomenclature is that such a particle will display properties which can be either liquid or solid, depending upon the time scale involved. For instance, a diffraction experiment will only see the atomic configuration over very short time scales, and measures a crystalline solid whereas on longer time scales of seconds the particle will move around like a liquid drop.

The transition from an experimentally static structure to one which fluctuates is not really a phase transition in any conventional sense. A somewhat better description is that of coexistence phenomena associated with a relatively soft configurational energy surface. Thermodynamically, at very low temperatures a particle will occupy the lowest energy structure. As the temperature is raised higher-energy structures become possible. Although the energy increases due to these higher-energy structures, this is offset by an entropy of mixing; the free energy of the 'phase', defined here as a set of coexisting structures, drops. For large particles the energy as a function of particle configuration is such a sharp function that the entropy of mixing contribution is swamped; at small sizes the energy variation is much softer so the entropy of mixing terms become significant. This is in essence the same model developed by Berry in a number of papers mentioned above to describe coexistence of liquid and solid states in very small clusters observed in molecular dynamics simulations and the standard broadening of a first-order phase transition by finite size effects. It should be noted that all that is required for such coexistence phenomena is a soft configurational energy surface.

Extending this approach further led to the concept of a phase map (figure 24) for particle structures versus size and temperature which includes this so-called quasi-molten state where the particles are changing structure (Ajayan and Marks 1988, 1990). There is some experimental evidence for, at least qualitatively, such a phase map. Hall (1991), Hall *et al* (1991), Reinhard *et al* (1993) and Patil *et al* (1993) have observed that at higher temperatures single crystals appear to be favoured over multiply twinned particles, consistent with the phase map. However Renou and Rudra (1985) report a conflicting result with MTPs *observed only at lower temperatures. It would be fair to state that the phase map needs* more experimental testing.

At the moment, details of the kinetics of the transitions in the quasi-molten state are sparse. It is generally observed that it occurs faster at higher temperatures, higher electron beam fluxes and when there is a weaker coupling to the substrate. An initial analysis (Narayanaswamy and Marks 1993) as shown in figures 25 and 26 has indicated that there is both rotational and conformational changes taking place, and very similar data limited to just the conformational changes have been reported by Kizuka *et al* (1993). Both these analyses indicate that the transitions between structures are relatively fast, i.e. fractions of a second, compared to the dwell time in a given structure which is of the order of seconds.

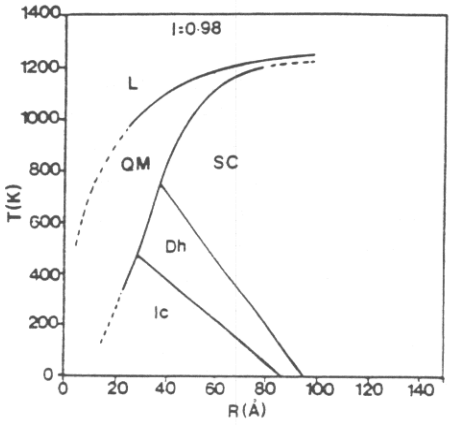

Figure 24. Phase map for small gold particles showing both the phase boundaries between single crystals and both types of MTPs and the coexistence of quasi-molten phase.

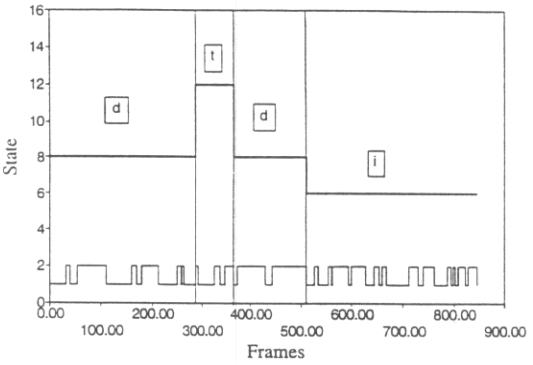

Figure 25. Real-time structural evolution during quasi-melting. The upper curve shows the different structures observed as a function of time, with d for decahedral MTP, t a twinned particle and i an icosahedral MTP. The lower curve shows the much faster rotation processes taking place, as transitions between values of 1 and 2.

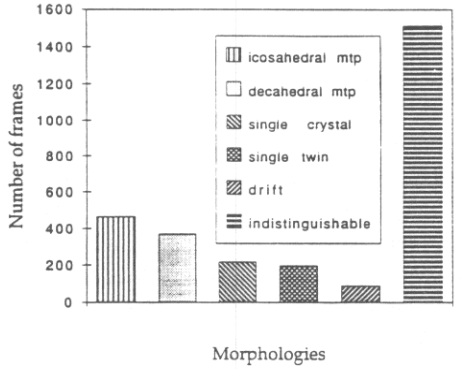

Figure 26. Statistics of a single particle during quasi-melting.

5.3. Surface fluctuations and surface melting

At a smaller scale, it is now well documented that the surface structures of small particles are not stationary on the time scales of electron microscope observations (seconds). Starting from the earliest work using the profile imaging technique (Marks and Smith 1983b), single atom (Wallenberg *et al* 1985), columns of atoms (Smith and Marks 1985, Malm and Bovin 1988) as shown in figure 27 and what has been called 'clouds of atoms' (Iijima and Ichihashi 1985, Bovin *et al* 1985, Kamino *et al* 1990) have been observed. Motion of atoms is not particularly surprising; in some respects it is surprising that the surfaces appear stationary enough for clear observation. Co-operative motion of atoms is a little more surprising, but

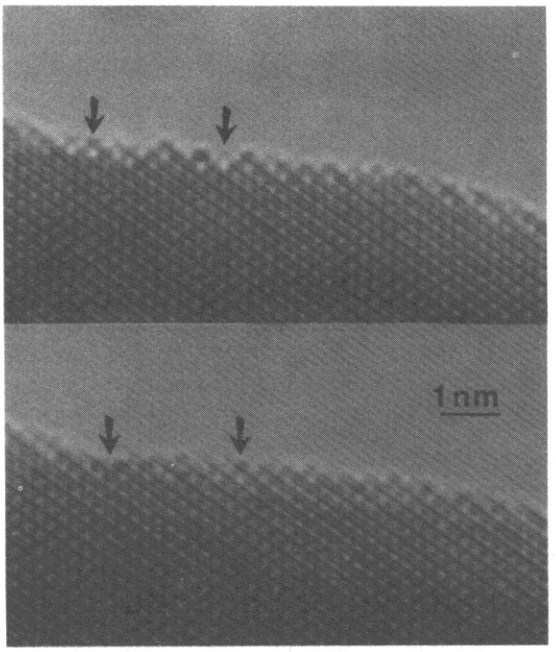

Figure 27. Two high-resolution images of a gold surface taken within a short time period. Atomic columns marked by the arrows have moved.

there are analogues of this in the surface science literature (e.g. Kellogg and Feibelman 1990, Ehrlich 1991, Kellogg and Voter 1991, Kellogg 1993) where surface displacement takes place by a replacement mechanism. The so-called atomic clouds have been modelled as small liquid or possibly solid particles rapidly fluctuating in structure (Wallenberg 1987), although a theoretical explanation is currently lacking. A phenomenon which appears to be relatively similar has been recently reported in molecular dynamics calculations by Cheng and Berry (1991, 1992) and Kunz and Berry (1993), a form of localized surface melting. It seems likely that many of these dynamic effects are intrinsically the same, thermodynamically, as coexistence of structures and/or liquid and solid particles as discussed in the previous section. Additional experimental information of these fluctuations can be found in the PhD Theses of Wallenberg (1987), Ajayan (1989) and Malm (1991).

There are also indications of surface reconstructions and even surface melting. For instance, under ultra-high vacuum (UHV) conditions the (001) facets of small gold particles have been observed to reconstruct into a mixture of a 3×1 and a 5×1 structure (Mitome *et al* 1991). The structures observed are not necessarily the same as those found in larger sized surfaces due to finite-size effects in the homo-epitaxy, similar to the changes in lattice parameter with size observed by Vincent (1968) and Heinemann *et al* (1983). Surface melting has also been proposed based upon both simulations with lead (Lim *et al* 1993) and experimental evidence from dark field electron microscopy (Lereah *et al* 1990). (Although the existence of such an effect is quite plausible, at the present moment the experimental evidence is not very strong.)

It seems fair to summarize these observations as indicating that the surface, similar to the particle as a whole, is not a static entity but evolves with time. Unfortunately, to date the only available data are observations of dynamic effects at surfaces, not quantification of them which makes further progress difficult.

5.4. Melting of small particles

Depression of the melting point in small particles can be traced at least as far back as

Thompson (1888) and the experimental work of Takagi (1954). I will not attempt here to review this particular topic, one of the oldest areas of small particle research. There is a fairly extensive literature on phenomena close to the melting point, which have commonly been interpreted as melting, see for instance Buffat (1976), the review by Kofman *et al* (1990), and the recent work by Castro *et al* (1990) at very small sizes and for semiconductor nanocrystals by Goldstein *et al* (1992). For instance, loss of diffraction intensity in dark field, flickering of spots as well as apparent melting have been reported. The majority of the observations are consistent with a depression of the melting point in most materials, although some elements do not seem to show this phenomena.

One issue that is somewhat unclear is where to draw the line between structural fluctuations and liquefaction of a small particle, a point also raised by Iijima and Ichihashi (1986); the two differ only on the time scale over which the particle is not crystalline and could easily be confused. Two short examples from the literature are appropriate. Allen *et al* (1986) note fluctuations in the contrast of small lead particles at temperatures as low as 26 C, an effect that Stowell *et al* (1970) also noted with small liquid lead particles at higher temperatures. Stowell *et al* (1970) also observed a very strong effect of the beam on the nucleation density of the lead; in the presence of the beam it increased by a factor of fifty. At least for lead particles it is clear that there is more taking place due to the electron beam than can be simply accounted for by any type of electron beam heating.

Another worrying issue is the effect of contamination upon the experimental results. A particularly relevant paper in this respect is that of Allen *et al* (1986). These authors report noticeable increases of the melting point of small particles under conditions (for tin) where tin oxide was observed in diffraction patterns. Since diffraction patterns are only weakly sensitive to oxide coverages, one cannot rule out monolayer contamination levels even in the cleanest experiments considering that elements such as lead and tin are highly reactive, even in a UHV environment.

6. Statics versus dynamics

Merging the numerous experimental observations of dynamic phenomena in small particles with the extensive body of static data is complicated. I want to describe here a fairly general model for this, including both thermodynamic and kinetic factors, which builds upon some of the earlier ideas of a structure map for small particles (Marks 1986b) and the phase map concept.

Statistical thermodynamics indicates that if we analyse a single particle for long enough, it will display all possible configurations with a probability distribution (relative occupancy time) given by the statistical distribution of

$$P(C) = \exp(-G(C)/kT) / \int \exp(-G(C)/kT)\,\mathrm{d}C \tag{22}$$

and C represents a given configuration and $G(C)$ is the free energy of a given particle configuration. If there is a global minimum in the free energy as a function of configuration and no local minima, the system will preferentially occupy the lowest energy state. Many of the earlier publications looking either for the lowest energy configuration or a size where MTPs converted to single crystals implicitly made this assumption. However, the fact that no single structure was present at a given size means that there are local minima.

An alternative approach is to consider that kinetics, rather than thermodynamics is the deciding issue. In this approach MTPs occur due to (kinetic) growth errors. However,

this approach cannot be defended any longer since particles can change their structure as discussed earlier.

The only approach which can rationalize at least the static experimental data is a potential energy surface with many local minima. Now it is possible to understand the plurality of static small particle structures as a representation of the local minima, and structural fluctuations of the particle as a whole as a coexistence of different configurations. Indeed, one can tentatively explain the various surface fluctuation phenomena along the same lines as coexistence phenomena. Can we further rationalize all the dynamic data with the same generalized model?

At least in very broad terms, this is possible. One can talk about a generalized, very qualitative Hamiltonian for a small particle of form

$$H = \sum_i p_i^2/2m + V_p(C) + V_s(C) + \eta \tag{23}$$

where p_i is the momentum of the i atom in the particle, $V_p(C)$ is the potential energy of the particle for a given configuration, $V_s(C)$ is the potential energy of the particle adhering onto the substrate, and η includes energy fluctuation terms such as adsorption of a phonon by the particle (from the substrate), energy from the electron beam and dissipative processes such as radiative losses. This type of Hamiltonian in a classical form is used in molecular dynamics simulations of small particles with the energy fluctuations coming from a heat bath. Depending upon the temperature, the particle will either remain in one state or dynamically move among them. Lowering the temperature leads to the well known simulated annealing algorithm.

Experimentally, if the electron beam flux is small we just consider thermal fluctuation effects. If the electron beam flux is substantial, it will contribute to the terms η and $V_p(C)$ in many different ways. In fact all the models proposed to explain small particle structure changes can be described by the above equation. For instance, core excitations can be considered as large spike injections of energy into the system. Transient charging is also possible, and could couple to motion of the atoms. Similarly, local change in the electronic state will produce transient changes in $V_p(C)$. There is also an obvious role for the substrate adhesion, and the thermal temperature. A *necessary* condition for structural fluctuations is that the potential energy surface is soft; a *sufficient* condition is that there are also sufficient fluctuations from whatever source to overcome the activation energy barriers.

There is additional evidence for this type of interpretation. It is relevant that with this same general framework, one can rationalize some of the phenomena observed with small particles by Stowell *et al* (1970). Describing the electron beam as a general pump of fluctuations, an increase in nucleation density as well as enhanced fluctuations of liquid particles is reasonable. In some additional, unrelated work (Ai *et al* 1993, Marks *et al* 1993, Volpert *et al* 1993) looking at oxygen desorption induced by the electron beam from transition metal oxides, very good evidence for enhanced point defect diffusion has been observed which can again be described as a fluctuation pump.

Combining these two models, we can at least qualitatively start to explain the diversity of small particle structures found. The distribution of particle morphologies and structures observed in a given experiment will reflect the statistical time evolution of many particles each governed by the type of equations described above, both during their active growth and since that time. The final distribution will be determined not simply by the relative energies (thermodynamics) of the different structures, but also the magnitudes of the energy barriers between different structures and the kinetics of structural changes. Two extreme cases of this model can be qualitatively solved:

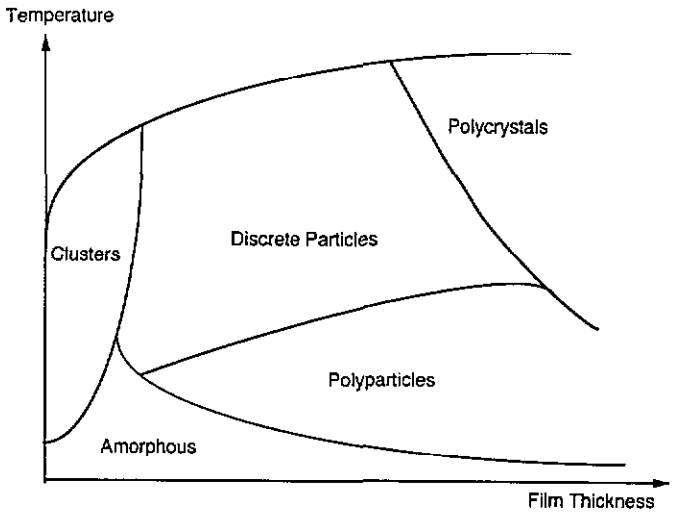

Figure 28. Schematic diagram of the different particle morphologies that could occur as a function of temperature and film thickness assuming that kinetic factors dominate the growth, taken from Marks (1986b).

(a) During the growth period the differences between the relative energies become larger as, say, the particle sizes increase but the kinetics of the transformations remain fast. Such a system should tend to evolve along a classical thermodynamic route yielding eventually just one type of particle. In this case the evolution of particle morphologies as a function of temperature can be represented as some sort of trajectory across a phase map such as that shown in figure 24. (It should be remembered that the phase map will be sensitive both to the substrate and the gas-phase environment.)

(b) During the growth period the activation energy barriers between different types of particles become larger and consequently the kinetics of transformations slow down but the relative energy differences remain quite small. In this case the particle population will be some sort of frozen representation (quench) of the distribution at the size when the kinetics became very slow. Further growth around these quenched structures with particle coalescence (but not recrystallization) has been discussed previously (Marks 1986b), and would lead to something similar to the structure map shown in figure 28.

A more complete analysis will almost certainly require addition of a third axis in addition to particle size and temperature, namely time. A hypothetical example of this is shown in figure 29 for cooling of a small particle of a given size from the liquid. The various lines in this diagram (what is called a Time–temperature–transformation or TTT diagram) would represent conditions where there is a 50% probability of a conversion from one form to another. Very rapid cooling could freeze in the liquid state as amorphous; slower cooling might initially lead to a single crystal. For the case drawn a decahedral MTP is more stable than a single crystal below a certain temperature, but the probability of a transformation is strongly temperature dependent; at higher temperatures the driving force for the transformation is smaller, at lower temperatures the kinetics will be slower leading to a characteristic 'C' shape.

The exact details of the growth process will also play an important part in this. For instance, if the particles are growing by some sort of supply of single atoms (e.g. evaporation) the two extreme cases above are probably representative. Alternatively, if

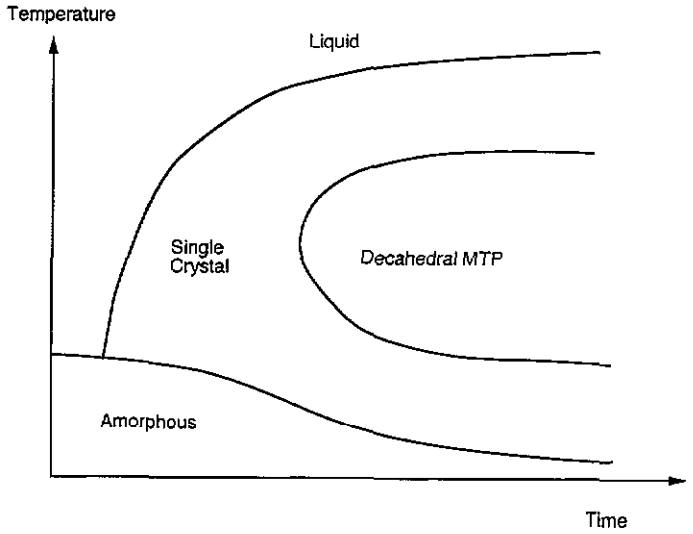

Figure 29. Schematic time-temperature-transformation diagram for cooling of a small particle as described in the text. The x, time axis here is logarithmic.

atom-exchange between clusters is important, i.e. Ostwald ripening is taking place (e.g. Voorhees 1992), the derivative of the energies of different morphologies with respect to their volume will enter the problem. (The rate of growth of one particle relative to others by exchange of atoms depends upon this derivative rather than the absolute free energy.)

The various phases and boundaries in figures 24, 28 and 29 are not at all clear and such diagrams may well be vast oversimplifications. However, the general framework for understanding small particle structures that they represent appears to be fairly consistent with the existing experimental evidence.

7. Discussion

During the process of reading papers for this review article, it has become apparent to me that some issues concerning small particle structures are now relatively well established. The most common structure is a single crystal and these are almost always close in shape to Wulff constructions. The next most common structure is probably simple twins, although there is rarely any publication of statistical data of particle populations. Of rather lower probability except for gold and silver is multiply-twinned particles.

The number of publications on multiply twinned particles is quite enormous, although many of them are little more than reports of their presence. In a few cases these particles are quite sharp icosahedra or decahedra, but the more common observation is of particles a little more rounder; the sharp structures are almost certainly due to kinetic factors in the growth. In general the decahedral particles seem to match the experimental and theoretical work of the author (Marks 1984), and both this continuum model and the atomistic analysis by Cleveland and Landman (1991) indicate that this is the appropriate local minimum energy configuration. It is also very clear that the fact that these particles are observed (or not observed) does not by itself indicate that they are the lowest energy configurations at a given size. The original idea of Ino (1966, 1969) that there is a certain size above

which they are not present seems to have been disproved; the real issue is the kinetics of a transformation from an MTP to a single crystal coupled with the growth kinetics.

There is also exceedingly strong evidence for the general idea of Wulff construction or modified Wulff construction shapes as (except at small sizes) size-independent structures. The most definitive proof of this for single crystals is the work of Heyraud and Metois (1983). The author has to acknowledge some personal bias, but the use by Haluska *et al* (1993) of the authors 1983 model (Marks 1983a) to explain the structure of millimeter sized fullerene crystals is quite startling when one considers that the original analysis was to explain particles five orders-of- magnitude smaller.

There also seems to be quite reasonable evidence for deviations from the conventional Wulff construction shape from the experimental data of Bonevich (1989, 1991) and the calculations of Cleveland and Landman (1991). Physically this must be the case, but further work is really needed to definitively check this in more detail.

In terms of the effect of conditions, both temperature and chemisorption, it is very clear that these are important although to date there is uncertainty about the details of their effects.

There is also strong evidence for deviations in many of the standard crystallographic parameters in small particles, for instance the lattice parameters and the Debye–Waller atomic vibrations. A caveat to these, unfortunately, is that being relatively weak effects they can also be strongly effected by uncontrolled surface conditions.

The idea that small particle structures are determined statistically, rather than every particle having the same structure is also inescapable from the experimental data. Exactly how to handle this in principle is obvious, but in practice difficult. Again with some personal prejudice, the structural fluctuations observed experimentally may be an important experimental probe particularly if the kinetics can be quantified.

There also seems to be a growing body of data from both experiments and computer simulations for coexistence phenomena both of different atomic arrangements and of small regions of the surface. In the view of the author coexistence of liquid and solid particles, coexistence of different particle morphologies and the various dynamic effects observed at surfaces are all fundamentally the same.

A final comment is more an appeal to authors as to how experimental data should be presented. Since no two particles are ever exactly the same, it would be much more informative if what was presented was quantification of the statistics of, for instance:

(a) The different particle morphologies versus size
(b) Coverage of different surface facets versus both size and morphology
(c) Both the above as a function, if appropriate, of conditions.

Hard experimental data of this sort replacing the more standard example images seems to be essential, and will be the only method of testing some of the ideas expressed in the previous section.

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