Equilibrium shape of a buoyant particle

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The equilibrium shape of a small particle on a substrate where the particle can sink into the substrate is evaluated.

I. INTRODUCTION

Small particles on supports have been of interest for many years both scientifically and with respect to their uses in heterogeneous catalysis. One of the common and often critical questions is the shape of a small particle, i.e., spherical or faceted, since many of the properties depend upon the relative populations of different surface planes and edges. The question of the equilibrium shape of an unsupported small particle was solved many years ago first by Wulff,[1] with later theoretical proofs in a continuum model by von Laue[2] and Dinghas[3] (see also Herring[4]). The extension to a supported particle on an infinitely flat substrate was given by Winterbottom,[5] and to twinned particles by Marks.[6,7] However, in all of these models to date the substrate has either been ignored or assumed to be infinitely flat and this latter assumption is really very dubious; in any real system diffusion can as easily change the substrate as the particle, and one should include this possibility. In some recent experimental work on small gold particles on MgO[8] we observed that indeed the substrate can change, and there are indications that a small particle can 'sink' into a substrate; see, for instance, Fig. 1. (We feel that it is useful to draw analogies to particles floating on a liquid and in this sense we will use the idea of sinking and buoyancy. Of course, gravity is not playing any role in the physics of the process.) As part of this work we employed a very simplified model to explain the physical source of sinking as an intermediate between the particle wetting the substrate and the substrate wetting the particle.

The purpose of this paper is to improve upon the theoretical model, and consider explicitly the equilibrium shape of a particle where the particle can partially sink into the substrate, i.e., a buoyant particle. In general, the problem does not appear to have a simple analytical solution, but we will show that with some assumptions about the directional dependence of the surface free energies it can be solved in a closed form by using an approach previously introduced for twinned particles by one of us.[6,7]

II. ANALYSIS

The problem that we are concerned with is the equilibrium shape of a small particle when we are specifically including the possibility that the particle can partially sink into the substrate. We will specifically not consider the kinetics of the process for the moment, which could readily lead to quite different results. It is important to define our notation for the different free energy terms:

Γ—the free energy per unit area of the substrate, explicitly a function of the surface normal.

γ—the free energy per unit area of the particle, implicitly a function of the facet normal.

ξ—the free energy of creating an interface by joining a unit area of free particle surface and free substrate surface. This is also implicitly a function of the facet normal for a given epitaxial orientation, and is implicitly negative.

h_j—the normal distance to the j facet.

h_s—the normal distance to the substrate surface.

A_j—the area of the j facet.

A_s—the cross-sectional area of the particle in the substrate surface plane.

For the model we will employ two approximations:

(1) We will assume that the substrate is large compared to the size of the particle. With this approximation, one can readily show that the change in surface energy due to redistribution of the volume displaced by the particle of substrate material is of the order of $\Gamma V_p / V^{1/3}$ where V_p is the volume displaced and V the total substrate volume; this is small and can be neglected. This assumption should be valid in most real systems.

(2) We will assume that ξ and Γ are proportional to γ with proportionality constants independent of facet orientation. This is a relatively severe approximation, but without it no simple analytical solution appears to exist. Note that if we were to use a simple model, such as a broken bond model, this approximation is not too severe. We will later on discuss some of the possibilities if this assumption is relaxed.

Using an approach similar to that of van Laue,[2] we can write the problem to be solved as one of minimizing:

$$F = \sum \gamma_j A_j - \Gamma A_s - 2\lambda \sum h_j A_j \qquad (1)$$

See, for instance, Fig. 2. We now employ an approach similar in spirit to that used for a modified Wulff construction;[6,7] namely, we make a mathematical cut of the
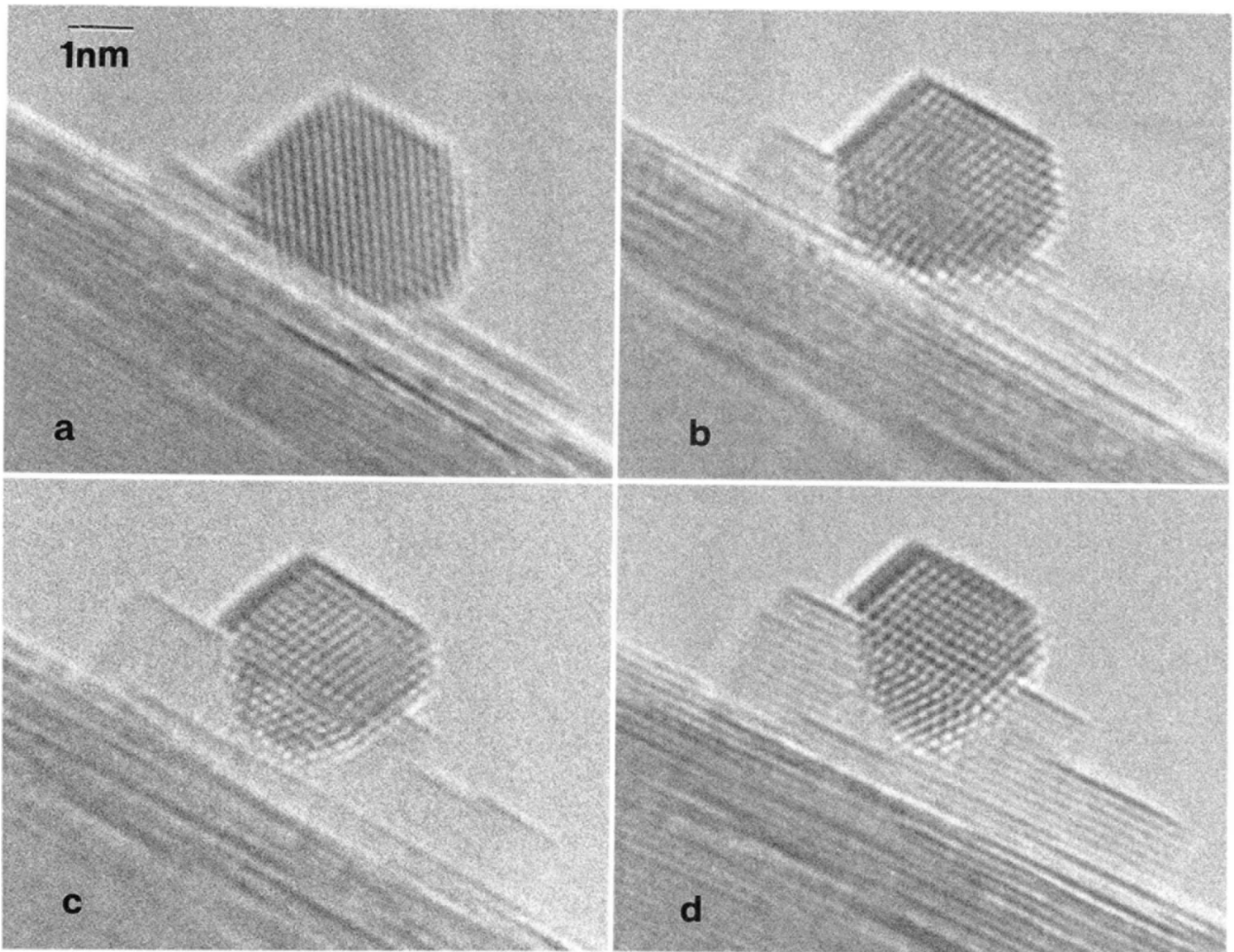
FIG. 1. High resolution electron microscopy images of a small gold particle sinking into MgO substrate material during 40 min of observation, taken from Ajayan and Marks.[8]

particle in the plane of the surface, partitioning the term involving Γ into two terms $\alpha\Gamma$ for below the substrate and $(1 - \alpha)\Gamma$ for above the substrate. We can then rewrite the problem as involving minimizing:

$$F = F_a + F_b \tag{2}$$

where F_a is for the region above the surface:

$$F_a = \sum \gamma_j A_j - (1 - \alpha)\Gamma A_s$$

$$- 2\lambda_a \left\{ \sum h_j A_j - h_s^a A_s \right\} \tag{3}$$

and F_b is for the region below the surface, i.e.:

$$F_b = \sum (\gamma_j + \xi_j + \Gamma_j) A_j - \alpha\Gamma A_s$$

$$- 2\lambda_b \left\{ \sum h_j A_j + h_s^b A_s \right\} \tag{4}$$

There are two possible types of solutions: either both

F_a and F_b are independently minimized or only the sum of the two. We will first consider independent minimization, which is simple since both Eqs. (3) and (4) are Wulff problems for which the solutions are given by:

$$\gamma_j = \lambda_a h_j \tag{5}$$

$$\gamma_j + \xi_j + \Gamma_j = \lambda_b h_j \tag{6}$$

$$(1 - \alpha)\Gamma = -\lambda_a h_s^a \tag{7}$$

$$\alpha\Gamma = -\lambda_b h_s^b \tag{8}$$

Equations (5)–(8) indicate that we have Wulff constructions for the top and bottom parts independently, but the scale of the two Wulff constructions can be different. To determine the relative scales, which is determined by the ratio of λ_a and λ_b, we require that the length of any facet which is common to both the top and bottom parts is the same, and that the two parts fit together. In general, the only way that the two parts can fit together is if the Wulff centers (after scaling by
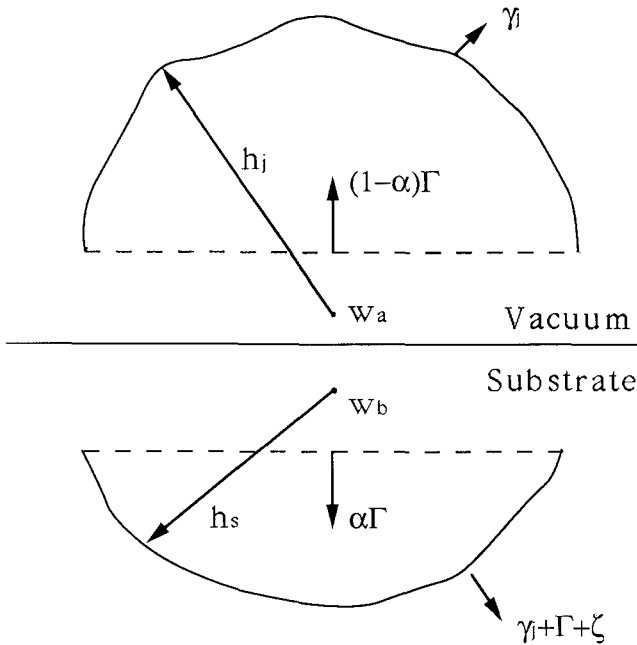
FIG. 2. Schematic of the construction used in the analysis of the free energy minimization problem, showing the decomposition of the particle into two parts. W_a and W_b are the independent Wulff centers for the top and bottom parts.

FIG. 3. Wulff construction solution to the problem with the approximations stated in the text.

λ_a, λ_b) are the same, in which case:

$$\lambda_b/\lambda_a = \gamma_i/(\gamma_i + \xi_i + \Gamma_i) \tag{9}$$

and

$$h_s^b = -h_s^a \tag{10}$$

$$\alpha = -\gamma_i/(\xi_i + \Gamma_i) \tag{11}$$

The shape that we have generated is in fact very simple; it is a Wulff construction for an isolated particle of unit scale ($\lambda_a = 1$) with the interface located a distance $\Gamma(\xi_i + \gamma_i + \Gamma_i)/(\xi_i + \Gamma_i)$ above the Wulff center; see Fig. 3.

We have found a stationary value of F; the question now is whether this is a true minimum, a saddle point, or a point of inflection. The minimization problem can also be written as minimizing $S/V^{2/3}$ where S and V are, respectively, the total surface free energy including the substrate term and the volume for top and bottom parts. For a true minimum, for any perturbation of the shape we require that

$$\delta S_a + \delta S_b > 2S(\delta V_a + \delta V_b)/3(V_a + V_b)$$
$$= 2(\delta V_a + \delta V_b) \tag{12}$$

(Note that for a Wulff construction of unit size $S = 3V$.) We can demonstrate that we have a true minimum by considering different types of deformations of the shape and showing that they all obey Eq. (12). There are three different types of deformation:

(1) A deformation of top or bottom only which does not alter the substrate cross-sectional area. This is
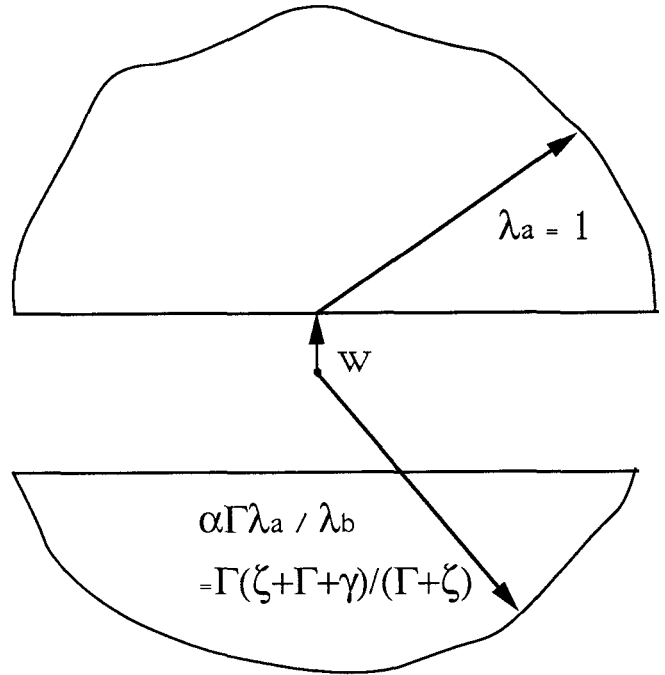
equivalent to a deformation of the vacuum Wulff construction and is therefore toward higher energy; see, for instance, Fig. 4.

(2) A deformation which changes the substrate intersection cross-sectional area and does not transfer volume between the top and bottom. This can always be treated (by rescaling) as a deformation which increases the volume V; see, for instance, Fig. 5. Independently, the top and bottom can both be considered as Winterbottom constructions which independently satisfy for a given value of the cut α

$$\delta S > 2S\delta V/3V \tag{13}$$

so that for this type of deformation the change in surface free energy is unconditionally positive and therefore,

$$\delta S_a + \delta S_b > (V_a\delta S_a + V_b\delta S_b)/(V_a + V_b)$$
$$> 2S(\delta V_a + \delta V_b)/(V_a + V_b) \tag{14}$$

which is toward higher energy.

(3) The only possible remaining deformation is one which involves movement of the effective substrate height (Fig. 6)—in other words, transfers volume from the top to the bottom or vice versa. For the modified Wulff construction it was argued that for the analogous case where the substrate plane is replaced by a twin boundary, the fact that the twin boundary energy was small relative to the external facet free energy introduced a constraint which eliminated this mode of deformation. This constraint effect was proved by more detailed numerical calculations.[9,10] Here we can prove
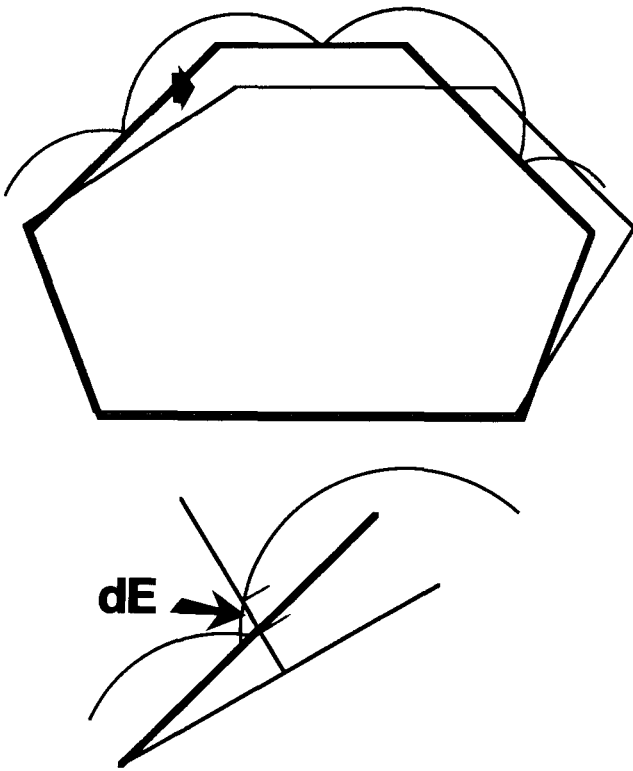
FIG. 4. Deformation of the top or bottom only which is mathematically equivalent to a deformation of the vacuum Wulff construction, resulting in an increase in energy dE.

the existence of a minimum more strongly. This type of deformation is equivalent to moving the substrate height with respect to the Wulff center, plus some changes to the outer surface. All components of the deformation in addition to moving the substrate height are toward higher energy since they can be considered as deformation types (a) or (b) above. Therefore the only possible mode of this deformation which could reduce the surface free energy is moving the substrate height without any other shape changes, which is a deformation at constant volume. Considering a motion of the substrate plane upward by δh, the change in the surface free energy due to the outer surface can be written as

$$dS/dh = \sum(\gamma_i + \xi_i + \Gamma_i)\,dA_i/dh$$
$$+ \sum \gamma_i\,dA_i/dh - \Gamma dA_s/dh \tag{15}$$

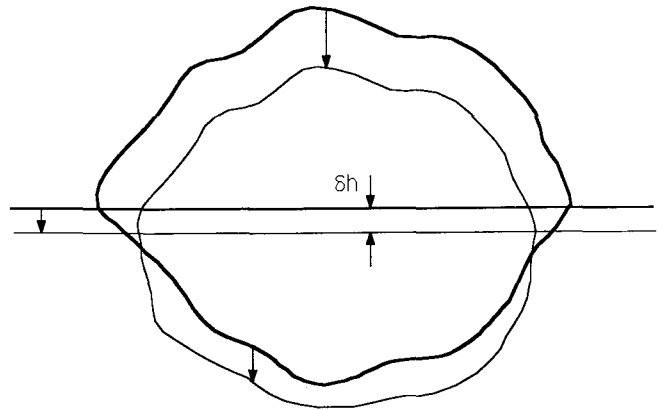FIG. 5. Deformation of the substrate cross section, which can be treated as a volume increase of δV by rescaling.

FIG. 6. Deformation involving movement of the substrate position with respect to the particle.

Using $\sum h_i dA_i/dh_k = A_k$, see Dinghas[2] \tag{16}

$$dS/dh = \{(\xi_i + \Gamma_i)/\gamma_i\}A_s$$
$$- (\Gamma + h_s^b[(\xi_i + \Gamma_i)/\gamma_i]\,dA_s/dh \tag{17}$$

so that

$$d^2S/dh^2 = -(\Gamma + h_s^b[(\xi_i + \Gamma_i)/\gamma_i]\,d^2A_s/dh^2) \tag{18}$$

or at the stationary modified-Wulff value

$$d^2S/dh^2 = -\Gamma(1 + [(\xi_i + \Gamma_i + \gamma_i)/\gamma_i]\,d^2A_s/dh^2 \tag{19}$$

Since A_s and Γ are positive, and for a convex Wulff construction the second derivative is always negative, then if $(\xi_i + \Gamma_i + \gamma_i)/\gamma_i > -1$ the solution is always a minimum. Note that $(\xi_i + \Gamma_i + \gamma_i)/\gamma_i < -1$ implies that the adhesion between the particle and substrate is sufficiently strong that it is more favorable for the particle to be completely buried by (sink into the) substrate. This condition is a little too strong, and from Eq. (9) we can place better limits on the solution, namely:

$(\xi_i + \Gamma_i + \gamma_i)/\gamma_i < -1$	Particle buried in the substrate (20)
$0 < (\xi_i + \Gamma_i + \gamma_i)/\gamma_i > -1$	Top surface only exposed (21)
$(\xi_i + \Gamma_i + \gamma_i)/\gamma_i > 0$	Buoyant particle (22)
$(\xi_i + \Gamma_i + \gamma_i)/\gamma_i \to \infty$	Particle floating on the substrate (23)
$(\Gamma_i + 2\gamma_i) < 0$	Particle wets the substrate (24)

Since all possible deformations of the shape are toward higher energy, we have proved that the shape generated previously is a minimum.

III. DISCUSSION

With the above analysis we have solved, albeit for a restricted set of surface free energy conditions, the

equilibrium shape of a buoyant small particle. In addition to conditions for particle wetting the substrate and the substrate wetting the particle, the real shape of a particle in equilibrium is partially submerged into the substrate. It is very important to stress that we are considering the equilibrium shape of a particle, and there are numerous physical constraints on achieving equilibrium; the particle must be in equilibrium with its vapor and the single atom population on the substrate and the substrate must be in equilibrium with its vapor. As perhaps most clearly demonstrated by Metois and Heyraud,[11] equilibrium is only occasionally reached. The same conclusion can be drawn from our own experiments; see, for instance, Fig. 1. Thermodynamically, the results in the figure do not correspond to minimizing the MgO surface free energy, but the kinetics of the process are dominating the process. The kinetics are going to be dominated by the relative speeds of surface and bulk diffusion of the substrate, and depending upon these we can envisage a number of different kinetic routes, as illustrated in Fig. 7. Clearly, this would be a good problem for numerical simulations. Despite this, the results shown are in fact in reasonable agreement with the theoretical predictions. For in-

FIG. 8. Tracing of the particle in Fig. 1(c), showing that there is an approximate Wulff center. The tracing has an error of ± atomic layer.

stance, shown in Fig. 8 is a tracing of the particle in Fig. 1(b), which indicates that there is close to a true Wulff center for the particle.

What about the situation when the conditions for the surface free energies are relaxed? We can here draw from the arguments used for the Modified Wulff construction.[7] We can represent the energy as a function of shape as a potential energy surface with a constraint that the top and bottom segments fit together. Rather than one simple minimum without the constraint, we can have a whole family of minima in the presence of the constraint. In fact, it does not follow that there exists one simple minimum at all; there may very well be many. We would draw here from our experience to date in calculating parts of this potential energy surface,[9,10] which clearly demonstrated that this is the case. In addition, the experimental results also support this conclusion; in Fig. 1 the development of a twin in (c) and (d) can be clearly seen.

In conclusion, changes in the substrate should be taken into account when considering the equilibrium shape of a small particle. However, application of equilibrium theories to small particles should be done with substantial care since the correct approach to small particles is via a potential energy surface.
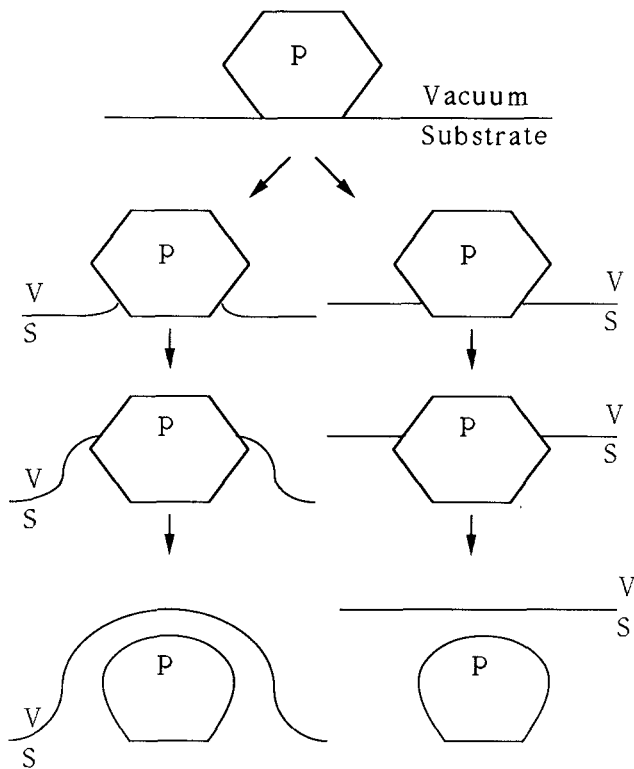

FIG. 7. Illustration of different kinetic paths for a particle sinking into a substrate. Depending upon the relative rates of surface and bulk diffusion, a floating particle might either 'sink' by being encapsulated by surface diffusion of the substrate or via bulk diffusion.
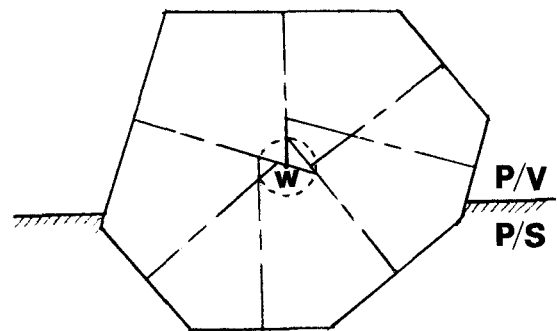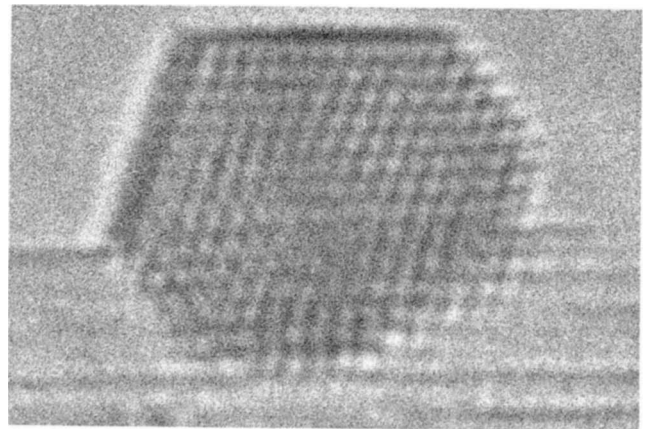
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