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Equilibrium Shapes of Crystals in a Gravitational Field: Crystals on a Table[1]

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We consider the variational problem associated with the equilibrium shape of crystals resting on a table in a gravitational field. For two-dimensional crystals the shape can be calculated explicitly, i.e., reduced to quadrature. In three dimensions only qualitative results are available. The most interesting new result is that for large crystals, under suitable conditions, the top may be a corrugated facet or curved surface. The motivation for this work comes from low-temperature experiments on helium crystals in equilibrium with the superfluid.

KEY WORDS: Equilibrium shapes; surface energy; gravity; crystals; calculus of variations.

1. INTRODUCTION

The ancient Greeks asked, and answered, the first question in the calculus of variations: What shape minimizes the surface for a fixed enclosed volume? It is the abstract version of the physical question: What is the equilibrium shape of, say, a small drop of water?

According to the rules of thermodynamics, the equilibrium shape minimizes the (free) energy. If the gravitational energy is neglected, as is reasonable for small objects, then minimizing the energy is equivalent to minimizing the surface energy. For liquids, the surface tension is a fixed

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(positive) constant, for fixed temperature, so minimizing the surface energy is equivalent to minimizing the surface area.

In this paper we consider the equilibrium shapes of crystals under gravity (or electric fields). For liquids this question was first analyzed by P. S. Laplace about a hundred and eighty years ago.[28] Crystals have an orientation-dependent surface tension so the surface energy is more complicated than just the area. Additionally, gravity is important or large objects. Our common experience is that small water droplets are roughly spherical but large ones form puddles.

One may cite several reasons for the increased difficulty of the problem when gravity is included. One is the loss of scale invariance: in the absence of gravity the volume acts merely as a scaling parameter. This is, of course, not true with gravity. Moreover, with gravity present the variational problem is not well defined until one specifies how the object is supported. It may rest on a table—the sessile drop[16]; it may hang from the tap—the pendant drop[45,46]; and it may cling to the windowpane (which requires dirt to act as a pinning force). All these cases are different.

Here we shall concentrate on the special case where the crystal is supported by a table. We choose a fixed crystal-table orientation, i.e., the angle between the crystal axis and the normal to the table is fixed.

Although a natural mathematical question, this is, of course, only a physical idealization. First, crystals may have excess energies associated with edges and corners[1] which we neglect (except for the estimation of the corrugation scale following Fig. 1 further). Second, we shall not consider effects due to elastic deformation of the crystal.[1] Third, the surface tension may depend explicitly on the gravitational field,[7] again something we shall not consider. Finally, and this is perhaps the most important point, large crystals are seldom in equilibrium. They tend to come in many shapes corresponding to metastable states separated by large energy barriers, compared to thermal fluctuation.[9,27,44]

We have been motivated by recent experiments on helium crystals in thermal equilibrium with the superfluid phase.[5-7,24,25] In these experiments it appears that the idealized model is reasonable. Thus, due to the large heat conductivity of the superfluid, and the smallness of the latent heat,

[7] The surface tension is determined, in principle, by statistical mechanics. For approximate realistic calculations see Ref. 8. Exact results are available for the two-dimensional Ising model,[38,39] and certain solid-on-solid three-dimensional models.[23] It is known that an external field changes some of the qualitative features of the surface tension,[44] so assuming the surface tension to be g independent is patently false. The statistical analysis of the surface tension with external fields (which we shall not consider here at all) turns out to be important also for questions related to adsorption.[34]

precise equilibrium can be obtained. The system is exceptionally pure, and due to the quantum nature of the solid, which leads, among other things, to large fluctuations even at low temperatures, it is conceivable that the crystal does not get stuck at a metastable ground state and shape.

We would like to recall the experiments of J. Landau *et al.*[(5,25)] and Keshishev *et al.*[(24)] Both experiments showed that certain facets disappeared and reappeared as the temperature was raised and lowered. This has been attributed to the roughening transition.[8,(5,7)] The experiments differ in important aspects, however. In the experiment of Keshishev *et al.* particular care was taken so that the crystal rested "horizontally" on the bottom of the cell. This was not the case in the experiment of J. Landau *et al.* In this experiment the crystal appeared to "droop" suddenly near the roughening temperatures. In the experiment of Keshishev *et al.*, the shape changed continuously with the temperature.

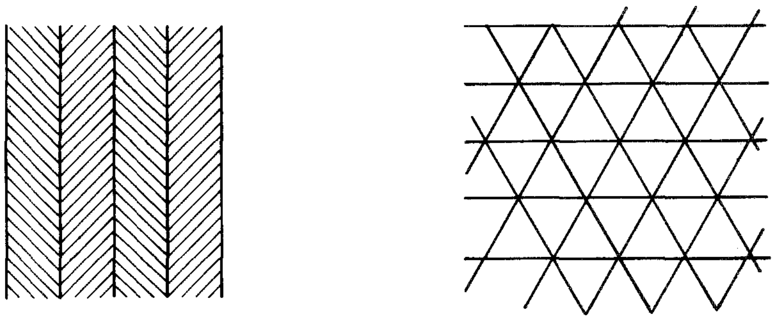
There are several questions that these experiments raise. Are the two experiments mutually consistent with regard to the sudden change in shape or are they just different? Does gravity affect qualitatively the roughening transition? Can gravity lead to the appearance of facets in directions where no facet existed for the $g = 0$ equilibrium shape? Can the presence of gravity cause facets to be pathological, e.g., nonsmooth?

Of interest is the relation between facets and step (free) energies. With zero gravity the free energy of steps is related to kinks (jumps in the derivatives) of the surface tension.[(21,29,43,44)] The roughening temperature is characterized by the vanishing of the step energy. A consequence of the Wulff construction is that a facet implies a positive step energy. In fact, a lower bound to the step free energy can be calculated from the area of the facet.[(44)] This is important because it provides a means, in principle at least, of measuring a critical exponent associated with the roughening transition.

Of course, with gravity present, the relation between the facet area and the step free energy is modified. We show that it is possible to have horizontal facets with zero step energy. Of course the surface tension is not an arbitrary function, and it might happen that statistical mechanics prevents this feature. It would be useful to know the answer.

Gravity can also induce new horizontal facets which are infinitesimally corrugated. This is a pathology. Two possible patterns of corrugation are shown in Fig 1. There is a simple intuition why corrugation can occur. Gravity favors flat tops while the surface tension may favor edges or corners pointing up.

[8] For a review see, e.g., Ref. 44.



(a) (b)

Fig. 1. Two possible patterns of corrugation for a horizontal facet in a gravitational field. (a) Grooves or furrows, (b) "meat tenderizer."

In actual crystals edges and corners have extra energies. These will make the corrugation finite. Thus if τ is the free energy per unit length associated with an edge the scale associated with the corrugation in Fig. 1a is of the order $(\tau l^2/\sigma)^{1/3}$, where l is the capillary length $l^2 \sim \sigma/\Delta\rho g$. τ/σ is typically of the order of few Å. The corrugation is of order of 10^{-3} cm if the capillary length is taken to be of the order of 1 mm. Similarly, if ν is the free energy of a corner the scale of Fig 1b is of the order $(\nu l/\sigma)^{1/3}$. ν/σ is of the order of few Å^2 so this scale is of order of about 10^{-6} cm if l is, again, of order 1 mm.

One would like to know if the equilibrium shape varies continuously with the parameters, temperature and pressure, or if there can be sudden changes analogous to first order phase transition. These questions are related to uniqueness.

Uniqueness is, of course, a natural mathematical question. Unfortunately, the answer is known only in the $g = 0$ case where uniqueness holds for general surface tension and for $g \neq 0$ where it holds for the sessile drop of liquid.[16] By a simple continuity argument, uniqueness then holds for small positive g's for general surface tensions and for all g for surface tension close to a constant (but, of course, not for negative g's when the energy functional becomes unbounded below). The question is, given σ, does uniqueness hold for the sessile crystal for all positive g? If the answer is affirmative, a crystal resting on a horizontal table will change its shape continuously with volume, and with continuous changes in σ due to changes in pressure and temperature. Discontinuous changes are then possible only if some of the parameters take certain boundary values; for example, if the crystal becomes unstable against forming a monolayer (complete wetting). Such first order phase transitions in liquids have been discussed in seminal theoretical and experimental works of J. Cahn.(11,32,35)

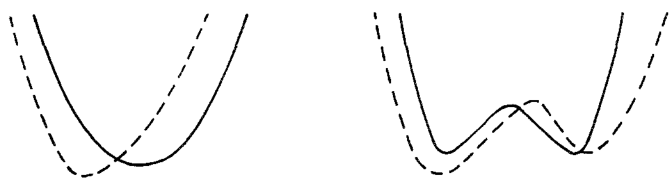
If the minimum is degenerate[9] for certain values of the parameters, the shape may change discontinuously at these values. This is L. D. Landau's argument(31) and it is illustrated in Fig. 2a, b.

For example, the shape of the pendant drop clearly can change discontinuously with the parameters: When the volume of water reaches a critical value the pendant drop drops. Here, of course, the mechanism leading to the discontinuity is not via degeneracy but rather uses the fact that the pendant drop is at a local minimum for the energy and there is no global minimum in Fig. 3.

Related cases where uniqueness is false, in general, are the equilibrium shapes of soap films: Plateau's problem.(2,3,14) Another familiar example,(13) taken from capillarity, is shown in Fig. 4.

An interesting possibility of "first-order" phase transition in capillarity of ^{4}He crystals was pointed out in Ref. 7.

One source of nonuniqueness for the sessile crystal lies in different patterns of infinitesimal corrugations. These may all have the same energy when the equilibrium shape has such a facet on top. The degeneracy may in fact be infinite. However, because the corrugation is infinitesimal all



(a) (b)

Fig. 2. Small changes in the energy functional lead to small changes in the location of the absolute minimum if it is unique (a), and may lead to discontinuous and large changes if the minimum is degenerate (b).

[9] Nondegeneracy is also related to the question of symmetry breaking. For example, it is not *a priori* obvious, although true, that the sessile drop is indeed cylindrically symmetric. Many examples of minimizing solutions whose symmetry is lower than that of the energy functional are given in L. Michel.(31) Of these, Jacobi and Poincare's treatment of the bifurcations taking place in the equilibrium shape of a rotating fluid is useful to keep in mind in the present context.

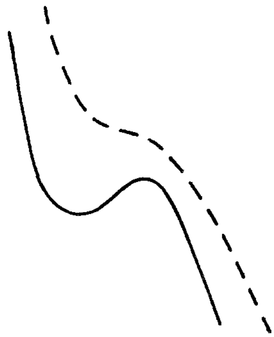


Fig. 3. Lack of continuity for the local minimum when the pendant drop drops.

Fig. 4. Discontinuous behavior of a liquid drop bounded by two wetted plates. The instability is associated with the up and down directions contributing negatively to the surface energy.

these shapes are macroscopically identical. In the latter sense it is still unique.

Recently R. Finn[16] gave a proof that guarantees uniqueness of the sessile drop in three dimensions. His method does not generalize for crystals since he uses the cylindrical symmetry of the drop to reduce the problem from a partial to an ordinary differential equation.

We have not resolved the question of uniqueness except in two dimensions.

The outline of this paper is as follows. In Section 2 we review the fundamental equations and constructions concerning this problem. In Section 3 we state our new results. In Section 4 we prove the results in the two dimensional case of a wetting crystal. In Section 5 we prove the results in three dimensions.

2. THE VARIATIONAL PROBLEM

In this section we shall review the variational problem for the equilibrium shape and some of its general properties. We shall derive the Euler–Lagrange equation for the equilibrium shape, and discuss Legendre transforms and their relevance. The fundamental equations have been worked out in 1951 by C. Herring.[20,21] Subsequent important contributions have been made by Cahn and Hoffman.[12,22]

The equilibrium shape is the minimum for the variational problem:[21,41]

$$E = \int \tilde{\sigma}(\hat{n})\,dS + \int \Phi(\mathbf{x})\,dV \tag{2.1}$$

subject to the fixed volume $V = \int dV$. The geometric objects dS, dV, $\hat{n}$, and $\mathbf{x}$ are, respectively, surface and volume elements, unit normal and a point on the surface. See Fig. 5. Φ is the gravitational potential energy. We define

$$\tilde{\sigma}(\hat{n}) = \begin{cases} \sigma(\hat{n}), & \hat{n} \neq -\hat{z} \\ \sigma_{12}, & \hat{n} = -\hat{z} \end{cases}$$

where $\sigma(\hat{n})$ is the surface tension of the crystal,[10] $[\sigma(\hat{n}) > 0]$ and $\sigma_{12} = \sigma_{CT} - \sigma_{MT}$. The subscripts C, M, and T refer to the crystal, medium, and table, respectively. We further assume[11] that $-\sigma(\hat{z}) < \sigma_{12} < \sigma(-\hat{z})$. The reason for this is that if $\sigma_{12} > \sigma(-\hat{z})$ it is advantageous for the crystal to insert an infinitesimal cushion separating it from the table. This is complete drying.[34,39,47] If $\sigma_{12} + \sigma(\hat{z}) < 0$ the crystal is unstable to forming a monolayer. This is complete wetting.[11]

If $\Phi = \nabla \cdot \mathbf{F}$ then (2.1) can be described as a surface integral only, namely,

$$E = \int \left[\tilde{\sigma}(\hat{n}) + \mathbf{F}(\mathbf{x}) \cdot \hat{n} \right] dS \tag{2.1a}$$

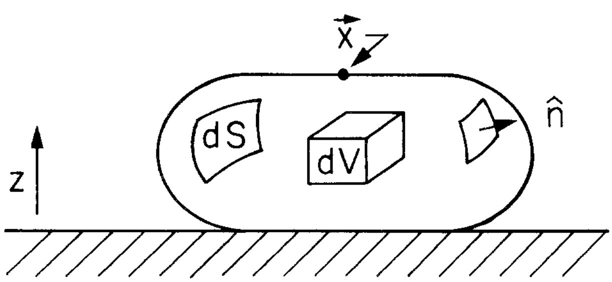


Fig. 5. The sessile crystal. $\hat{z}$ is the direction normal to the table; $\hat{n}$ is the normal to the surface of the crystal, dS the area infinitesimal and dV is the volume infinitesimal. $\mathbf{x}$ is a generic point of the crystal.

[10] In the thermodynamic limit, σ may lack smoothness. It has been shown by L. D. Landau that at zero temperature σ for a crystal may have kinks at all rational directions.[26]

[11] More precisely, we shall assume this inequality for the σ corresponding to the convexified f discussed below.

For a crystal resting on a horizontal table in a gravitational field

$$\Phi(\mathbf{x}) = \begin{cases} \infty, & z < 0 \\ (\rho_C - \rho_M)\mathbf{g} \cdot \mathbf{x}, & z \geqslant 0 \end{cases}$$

so that

$$\mathbf{F}(\mathbf{x}) = -(1/2)\Delta\rho(\mathbf{x} \cdot \mathbf{x})\mathbf{g}, \qquad z \geqslant 0 \tag{2.2}$$

Here g is the gravitational constant and $\Delta\rho$ the density difference $\rho_c - \rho_M$.

The variational problem for $g = 0$ and no table was formulated independently by W. Gibbs in 1878 and by P. Curie in 1885. It was solved by Wulff in 1904,[48] who gave the correct answer but a wrong proof. The history of the Wulff solution is quite complicated and amusing. The interested reader can find an account of it in C. Herring.[20,21] The chapter was more or less closed in 1944 when A. Dinghas gave a proof of the Wulff construction based on the Brunn–Minkowsky inequality.[21] The full generality of the result is due to Herring[20,21] and Taylor.[41,42] The Wulff–Dinghas solution has the following features: It is a succinct geometric construction; it gives a unique (convex) equilibrium shape; the shape scales with the volume; the shape is smooth in the same sense that polygons are smooth, i.e., it is smooth except for possibly a finite number of edges and corners. Finally, the shape depends continuously on the surface tension. Analytically, the Wulff construction without a table is the set $W = \{x : \mathbf{x} \cdot \hat{n} \leqslant \sigma(\hat{n})\}$. With a table present, the surface tension in the direction of the table, σ_{12}, being a difference, may be a negative number. This is a minor complication and the Wulff construction generalizes in the obvious way:[47]

$$W = \{x : \mathbf{x} \cdot \hat{n} \leqslant \tilde{\sigma}(\hat{n})\} \tag{2.3}$$

Geometrically, the Wulff construction, with a table present, is illustrated in Fig. 6.[21,47]

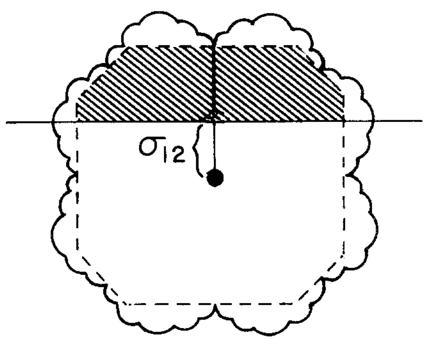


Fig. 6. The Wulff construction for a crystal on a table. The cloverleaf is the polar plot of the surface tension. The polygon (broken line) is the Wulff plot, and the equilibrium shape in free space. The hatched area is the shape for the crystal on a table with zero gravity.

We remark that, for $g = 0$, it is possible also to determine geometrically which orientation of the crystal has least energy. This follows from the observation that the energy is proportional to the hatched volume in Fig. 6, namely,[21,49]

$$E_{g=0} = 3\,W^{1/3}V^{2/3}$$

W is the volume of W.

If one expresses the shape in a parametric form[18] then, in three dimensions, the surface of the crystal is given by $\mathbf{x}(u, v)$, where (u, v) are two real parameters.

Let

$$\begin{aligned} \mathbf{N} &\equiv \partial_u \mathbf{x} \times \partial_v \mathbf{x} \\ f(\mathbf{N}) &\equiv |\mathbf{N}|\sigma(\hat{n}) \\ \tilde{f}(\mathbf{N}) &\equiv |\mathbf{N}|\tilde{\sigma}(\hat{n}) \end{aligned} \tag{2.4}$$

where

$$\begin{aligned} \hat{n} &= \mathbf{N}/|\mathbf{N}| \\ dS &= |\mathbf{N}|\, du\, dv \end{aligned}$$

The variational problem for the entire surface can be written as

$$\hat{E} = \int \left[\tilde{f}(\mathbf{N}) - (\lambda/3)\mathbf{N}\cdot\mathbf{x} + \mathbf{F}(\mathbf{x})\cdot\mathbf{N} \right] du\, dv \tag{2.5}$$

with $F(\mathbf{x})$ given in (2.2). λ is a Lagrange multiplier associated with the constraint of fixed volume.[12]

Equations (2.1) and (2.5) completely specify the problem, except that we have not specified what class of surfaces the functional is to vary over, namely, how wild $\mathbf{x}(u, v)$ are allowed. (See Refs. 33, 40, and 41 for these questions.) The Euler–Lagrange equations for (2.5) are

$$\partial_u \mathbf{x} \times \partial_v \nabla_{\mathbf{N}} \tilde{f}(\mathbf{N}) - \partial_v \mathbf{x} \times \partial_u \nabla_{\mathbf{N}} \tilde{f}(\mathbf{N}) = \left[\lambda - \Phi(\mathbf{x}) \right] \mathbf{N} \tag{2.6}$$

($\nabla_{\mathbf{N}}$ means the gradient with respect to the variable $\mathbf{N}$.) One verifies that from the homogeneity properties of $f(\mathbf{N})$ the transverse components of (2.6) are automatically satisfied, leaving only the component in the $\mathbf{N}$ direction,

$$2\nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{N}} \tilde{f}\left[\mathbf{N}(\mathbf{x}) \right] = \lambda - \Phi(\mathbf{x}) \tag{2.7}$$

Some simple differential geometry gives Herring's formula:

$$K_1\left[1 + (\hat{e}_1 \cdot \nabla_{\hat{n}})^2 \right]\sigma + K_2\left[1 + (\hat{e}_2 \cdot \nabla_{\hat{n}})^2 \right]\sigma = \lambda - \Phi(\mathbf{x}) \tag{2.7a}$$

[12] When $g = 0$ one has $\lambda = 2(W/V)^{1/3}$ with W given below. λ is therefore positive and decreasing with V. The positivity of λ holds in general. However, when $g \neq 0$, λ does not decrease to zero as $V \to \infty$, in fact, $\lambda \to \lambda_c = [2g\Delta\rho(\sigma(\hat{z}) + \sigma_{12})]^{1/2}$ as shown in Eq. (4.5) in two dimensions and Eq. (5.3) in three dimensions.

or equivalently

$$K_1[\hat{e}_1 \cdot \nabla_N]^2 f(N) + K_2[\hat{e}_2 \cdot \nabla_N]^2 f(N) = \lambda - \Phi(\mathbf{x}) \tag{2.7b}$$

where $K_{1,2}$ are the principle curvatures[13] and $\hat{e}_{1,2}$ the corresponding directions in the equilibrium shape.[12]

The geometric meaning of (2.7) was elucidated in 1951 by C. Herring.[20] Further developments are due to Cahn and Hoffman.[12,22] In particular, the latter were the first to note the naturalness of $\nabla_N f$ which they denoted $\boldsymbol{\xi}$. We shall later remark on the geometric meaning of $\boldsymbol{\xi}$ and its relation to Legendre transforms.

From the point of view of differential geometry there are two obvious choices for $\nabla_N \tilde{f}$ that would make the left hand side of (2.6) point in the $\hat{n}$ direction (in a neighborhood of $\hat{n}$).

(i) The first is $\nabla_N \tilde{f}[N(\mathbf{x})] = \text{const}(\mathbf{x} - \mathbf{x}_0)$ by Eq. (2.4). This is the analytic form of the Wulff construction (provided f is twice differentiable). It solves Eq. (2.6) for $\Phi(\mathbf{x})$ being a constant which is the case when $g = 0$.[4]

(ii) The second choice if $\nabla_N \tilde{f} = \text{const}\ \hat{n}$ which holds for liquids with no assumption on $\Phi(\mathbf{x})$. Here we make use of Ref. 17:

$$\partial_u \mathbf{x} \times \partial_v \hat{n} - \partial_v \mathbf{x} \times \partial_u \hat{n} = 2H\mathrm{N}$$

with H the mean (extrinsic) curvature. This gives the celebrated Young–Laplace formula[1,28]

$$2\sigma_0 H + \Phi(\mathbf{x}) = \lambda$$

with σ_0 the (constant) surface tension.

Equation (2.1) can be rewritten as

$$E = \int \vartheta(z)\left[f(\mathrm{N}) + \mathbf{F} \cdot \mathrm{N} + \sigma_{12}\mathrm{N} \cdot \hat{z}\right] du\, dv \tag{2.1b}$$

where $z \equiv x_3(u, v)$ is constrained to be positive and $\vartheta(z) = 1$ if $z > 0$ and 0 if $z \leqslant 0$.

Some simplification takes place when the shape can be described by a single-valued function $y(\mathbf{x}_\perp)$ representing the height of the crystal above the point $\mathbf{x}_\perp$ of the table. This is the case if the angles of contact are such that the crystal wets the surface. For Φ given by (2.2), (2.1) can be rewritten:

$$E[y] = \int d\mathbf{x}_\perp\, \vartheta(y)\left[\hat{f}(\mathbf{p}) + (1/2)g\Delta\rho y^2 + \sigma_{12}\right] \tag{2.8}$$

where

$$\mathbf{p} \equiv \nabla y \qquad \hat{f}(\mathbf{p}) \equiv \sigma(\hat{n})(1 + \mathbf{p}^2)^{1/2}, \qquad \hat{n} = (-\mathbf{p}, 1)/(1 + \mathbf{p}^2)^{1/2} \tag{2.9}$$

The volume is, of course, $V = \int y\, d\mathbf{x}_\perp$.

[13] K is defined to be positive for convex shapes.

Starting from Eq. (2.8), the Euler–Lagrange equation takes the simple form:

$$\sum \hat{f}_{ij} y_{ij} = \Delta\rho g y(\mathbf{x}) - \lambda$$

where $\hat{f}_{ij}$ denote partial derivatives with respect to p_i and p_j while y_{ij}, with respect to $\mathbf{x}_{\perp i}$ and $\mathbf{x}_{\perp j}$. Owing to the translation invariance of the gravitational potential in the horizontal directions, there exist conserved Noether currents:

$$\sum \partial_i J_{ij} = 0, \qquad J_{ij} = (\partial_{p_i} \hat{f})(\partial_{x_j} y) - \delta_{ij}\left[\hat{f} - \lambda y + (1/2)\Delta\rho g y^2\right]$$

Given f, let f^* be its convexification (the convex envelope of f, or, the smallest f with the same Wulff plot. See Fig. 7). A necessary condition for the stability of the minimizing surface is the positivity of the second variation of the total energy. Since areas and volumes scale differently, the direction $\hat{n}$ can occur as a true normal to the surface (as opposed to a normal to a varifold-type, infinitesimal sawtooth surface) only if it can also appear in a surface that minimizes the surface energy alone. The condition for every direction to be *a priori* possible as a true normal to the equilibrium shape, is then seen to be the convexity of f (and so $f = f^*$). If f is convex, and twice differentiable, the form $\partial_{N_i N_j} f$ is positive. If this form is positive definite f is said to be *elliptic*.[2,33] For a direction $\hat{n}$ which does not occur as a normal to the Wulff plot W, it is possible to have a surface with infinitesimal sawteeth, an apparent normal $\hat{n}$, and consequently the (smaller) surface tension corresponding to $f^*(\hat{n})$ rather than $f(\hat{n})$. It is thus never any loss to replace the surface tension function f by its convexifica-

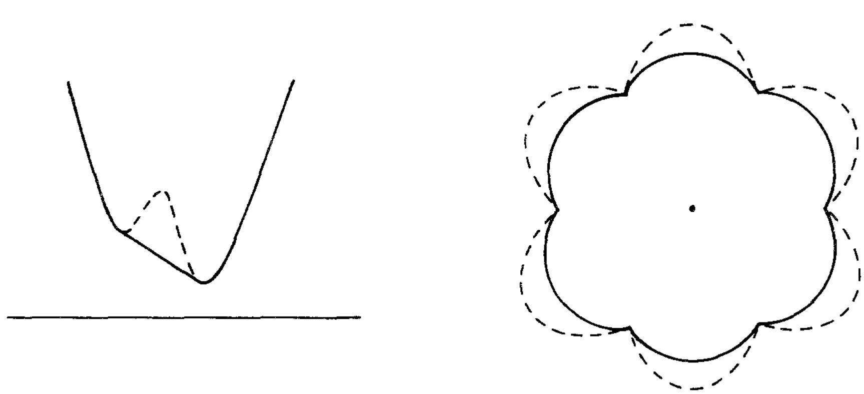


Fig. 7. The convexified f is shown in solid lines and the unconvexified f is shown in broken lines (on the left). The same for the polar plot of σ is shown on the right.

tion f^* in determining the overall geometry of the equilibrium shape.[41] This also avoids the necessity with dealing with varifold type solutions, though they remain of equal surface energy when non-Wulff shape normal directions are present.

V can be scaled to 1 by letting $g \to gV^{2/d}$ and $E \to EV^{(d-1)/d}$ with d the dimension. Because Eq. (2.5) has simple scaling properties (the transformation $\mathbf{x} \to \alpha\mathbf{x}$ takes $\mathbf{N} \to \alpha^{d-1}\mathbf{N}$, $f \to \alpha^{d-1}f$, $\Phi \to \alpha\Phi$, etc.) one has a "virial theorem"

$$d\lambda V = (d-1)E_S + (d+1)E_G \geqslant 0 \tag{2.10}$$

where $E_{S,G}$ denotes the surface and gravitational energy in equilibrium.

An application of the virial is the asymptotic of the height, h_∞, in the $V \to \infty$ limit. In this limit the principle curvatures at the top are expected to vanish. This relates λ and h_∞ via Herring's equation. E_S and E_G can be estimated by assuming the shape of a pillbox. Combining this with the virial gives a result which, for liquids, is originally due to Laplace[16,28]:

$$g\Delta\rho h_\infty^2 = 2[\sigma(\hat{z}) + \sigma_{12}]$$

It is an interesting observation of Laplace,[28] (see also Ref. 16) that at least for liquids, the height approaches h_∞ from above in the three-dimensional problem and from below in the two-dimensional one. We do not know of a simple explanation of the different behavior of two and three dimensions.

It was mentioned above that Legendre transforms enter naturally. In fact, the Wulff construction is nothing else than the Legendre transform, as we shall see below. The Legendre transform will also shed some light on why the vector equation (2.6) for the three unknown functions $\mathbf{x}$ can be reduced to the single scalar equation without loss.

For convex function $c(\mathbf{x})$, the Legendre transform, $C(\mathbf{N})$, is defined by

$$C(\mathbf{N}) = \max_{\mathbf{x}} [\mathbf{N} \cdot \mathbf{x} - c(\mathbf{x})].$$

It has the simple geometric meaning given in Fig. 8. $C(\mathbf{N})$ is then also convex. The Legendre transform is self-dual, namely, the transform of $C(\mathbf{N})$ is $c(\mathbf{x})$. If the original $c(\mathbf{x})$ was not convex $C(\mathbf{N})$ is still convex and its transform is $c^*(\mathbf{x})$ which is the convexified $c(X)$.

In general, the Legendre transform leads to the correspondence between smoothness for the function and strict convexity of the transform and vice versa. For example, the matrices $\partial_{N_i N_j} C(\mathbf{N})$ and $\partial_{x_i x_j} c(\mathbf{x})$ are inverse to each other at $\mathbf{N} = \nabla_x c(\mathbf{x})$.

To apply this machinery to the crystal shape problem, we associate with the crystal (which we assume to be a convex object) the function which is 0 inside the crystal and ∞ out of it. This function is convex. Its Legendre transform, $X(\mathbf{N})$, is known as the *support function*.[37]

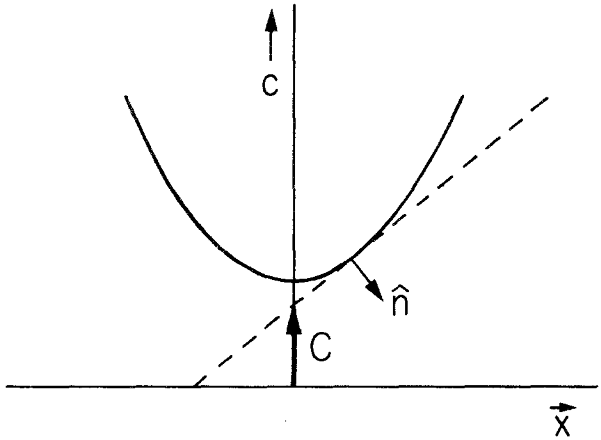


Fig. 8. The geometric meaning of the Legendre transform which associates $C(\hat{n})$ with $c(\mathbf{x})$.

Clearly,

$$X(\mathbf{N}) = \max_{\mathbf{x} \in V} \mathbf{x} \cdot \mathbf{N}$$

This relation can be inverted (assuming strict convexity) giving

$$\mathbf{x} = \nabla_{\mathbf{N}} X(\mathbf{N})$$

$X(\mathbf{N})$ is positively homogeneous of first degree so

$$X(\mathbf{N}) = |\mathbf{N}| q(\hat{n})$$

The upshot of this is that in Eq. (2.6) one may regard $\hat{n}$ as the *independent* variables and $q(\hat{n})$ as the *single* unknown function to be determined. Indeed, the Wulff construction with the table and convex f is the statement that

$$X(\mathbf{N}) = (2/\lambda)\left[f(\mathbf{N}) - \sigma_{12} \mathbf{N} \cdot \hat{z} \right] \tag{2.11}$$

3. NEW RESULTS

Without loss of generality, we assume throughout this section that f is convex. We also continue to use V to denote either an equilibrium shape for $g > 0$ or the volume of such a shape and with W the same for $g = 0$.

1. There exist solutions to the problem in the class of "(γ, δ)-restricted sets." This follows from techniques in Ref. 2, Theorem VI.2. The results as stated there have a hypothesis that f be a continuously differentia-

ble function; however, since f is a constant coefficient integrand the step in the proof where this is used can be by-passed by using dilations to regulate the volume rather than the deformations of VI.6.

2. Properties of E. The stability against complete wetting [i.e., $\sigma_{12} > -\sigma(\hat{z})$] guarantees that[14]

$$E_g \geqslant E_{g=0} > 0$$

The first inequality follows from the positivity of the gravitational energy and the second from the assumption of no complete wetting. From the scaling properties and the positivity of the gravitational energy one finds immediately that E is an increasing function of V. Since E is clearly subadditive, $E_{V_1+V_2} \leqslant E_{V_1} + E_{V_2}$, $E(V)$ is concave downward. λ is uniquely determined by V but not vice versa (see 4.1(ii) below).[15]

3. $\lambda \geqslant \Phi(\mathbf{x})$. From (2.7b) this is true at the top of the crystal. By the monotonicity of Φ it is then true everywhere (this is not really a new result).

4. From (3) and (2.7a, b) we conclude the following:

(a) The equilibrium shape for $g > 0$ can have facets (which implies $K_{1,2} = 0$) only in directions where $\tilde{f}^*$ is not twice differentiable (i.e., W has facets or edges), except that an additional horizontal facet is not ruled out if $\lambda = \max_{\mathbf{x} \in V} \Phi(\mathbf{x})$.

(b) Edges ($K_1 = \infty$) and corners ($K_{1,2} = \infty$) in V imply that the second derivative of f in the corresponding directions are zero, and again only occur in directions where edges and corners occur in the Wulff shape. (Note that we *cannot* conclude directly that if $\hat{n}$ does not occur as a normal to W, then it does not occur as a normal to V.)

5. We give a simple derivation of the contact angle equations. Upon differentiating the functional, Eq. (2.1b), one finds terms proportional to $\delta(z) = d_z \vartheta$. These give the boundary condition. Collecting these terms gives

$$\mathbf{N}(\sigma_{12} + \hat{z} \cdot \nabla_{\mathbf{N}} f) + \hat{z}[f(\mathbf{N}) - \mathbf{N} \cdot \nabla_{\mathbf{N}} f] = 0$$

Since $f(\mathbf{N})$ is positive homogeneous of first degree, this can be written as a

[14] E may fail to be positive, even without complete wetting if there is more than one direction where the surface tension is negative, e.g., Fig. 4.

[15] Because of the unique determination of λ by V, uniqueness for the variational problem with fixed V is given by uniqueness for the problem with fixed λ. Since the contact angles are uniquely determined the question is translated to the uniqueness of solutions to a certain nonlinear partial differential equation with prescribed boundary conditions. This is, unfortunately, a hard problem. In fact the route is often transversed in the opposite direction.[15,30,36] Namely, uniqueness of solutions of nonlinear differential equations can sometimes be shown by constructing a variational problem with a convex functional whose Euler–Lagrange equation is the requisite one. The variational problem posed here is clearly not convex if f is not convex. This is not a serious obstacle because, as argued above, f may be replaced by the convexified f^*. More serious is the $\vartheta(*)$ in Eq. (2.1b), which is not convex and cannot be argued away.

generalized Young–Dupre[1] equation

$$\sigma_{12} + \partial_{N_z} f(\mathbf{N}) = 0 \tag{3.1}$$

The solution for the contact angles can be given a geometric interpretation. Since Eq. (3.1) is independent of g, it is the solution given by the Wulff construction. Note that in solving for the Legendre transform $X(\mathbf{N})$, the boundary condition is

$$\partial_{N_z} X(\mathbf{N}) = 0$$

which can be written equivalently as Eq. (2.11).

6. In general dimensions, if f is elliptic, then there is no gravity induced faceting for any g (see Section 5 for proof).

7. If W is polyhedral and there is a corner [resp. an edge] pointing up in W, and if V is convex, then for large enough g relative to the volume of V there is a facet on top of V [resp., either there is a facet on top of V or V is curved near its top]. (See section 5 for the proof of these results.) (To show that V must be convex does not seem easy though it looks like a minimum within a class of convex sets can be shown to be a local minimum for E_g if W is polyhedral. The proof of these statements will not be given here, however.)

8. In two dimensions, and in the case that the surface is wet by the crystal, then (i) faceting is possible with large enough g provided f is not elliptic near $\hat{n} = \hat{z}$, (ii) solutions are unique and convex, and (iii) solutions are given explicitly by quadrature. (See the next section for proofs.)

4. SOLUTIONS IN TWO DIMENSIONS

Throughout this section we denote by f the function we called $\hat{f}$ in section 2 [Eq. (2.9)]. Also a factor of $\Delta\rho$ will be absorbed in g.

For a *wetting* crystal in two dimensions the equilibrium shape $y(x)$ can be solved by quadrature. The reason for that is that Euler–Lagrange equation $\ddot{y} \cdot f'' = gy - \lambda$ (where $\dot{y} = dy/dx$, $f' = df/dp$ and $p \equiv \dot{y}$) has a first integral associated with the invariance of the energy functional under translations in x. There is an exact analogy to ordinary Newtonian mechanics where time plays the role of x. In the latter, the integral expresses conservation of energy. In more than two dimensions one has, instead, conserved Noether currents. We did not get any mileage out of these so we restrict ourselves to two dimensions. One finds

$$k(p) + \lambda y - \tfrac{1}{2} g y^2 = \text{const}$$

where

$$k(p) \equiv p \cdot f'(p) - f(p) \tag{4.1}$$

Evaluating $k(p)$ at the end point and using the contact angle equation, we arrive at the requisite differential equation:

$$k(p) + \lambda y - \tfrac{1}{2} g y^2 - \sigma_{12} = 0 \tag{4.2}$$

4.1. Strictly Convex f with f' Differentiable

For this class of f, corresponding to each value of $k(p)$, there are only two values of p, one positive, the other negative. Furthermore, $k(p)$ is a continuous function.

Let us rewrite Eq. (4.2) as

$$\lambda y - \tfrac{1}{2} g y^2 = K(p) \equiv -k(p) + \sigma_{12} \tag{4.3}$$

and plot the two sides of the equation separately (Fig. 9a, b). In this form the left-hand side contains only the volume and gravity (surface) effects. Note that, for $\lambda \geqslant \lambda_c$, (4.3) can be satisfied by two values of p ($\equiv dy/dx$) for each value of y such that $0 \leqslant y < K(0)$. These two values of p correspond to the two sides of the crystal, of course. Clearly, for $\lambda < \lambda_c$, (4.1) cannot be satisfied in this manner for all $y \leqslant K(0)$. The explicit value of λ_c may be found from the graphs, or equivalently, from an explicit equation for h, the height. Now, let $h \equiv y$ $(p = 0)$ (4.3) implies that $\lambda h - (1/2)h^2 = K(0)$, so that

$$gh = \lambda - \left[\lambda^2 - 2gK(0)\right]^{1/2} \tag{4.4}$$

Replacing $K(0)$ by its value $\sigma[(0,1)] + \sigma_{12}$ one obtains, for this to be real,

$$\lambda \geqslant \lambda_c = \left\{2g\left[\sigma((0,1)) + \sigma_{12}\right]\right\}^{1/2} \tag{4.5}$$

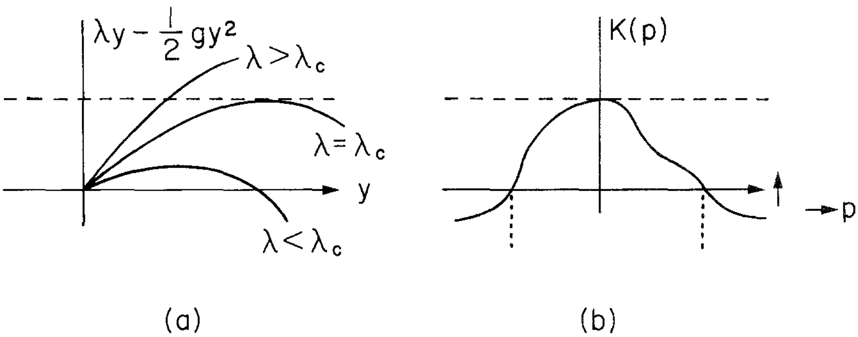


Fig. 9. (a) The left-hand side of Eq. (4.3) and (b) its right-hand side. The intersection with $K(p) = 0$ gives the contact angles.

We will show that, if $f'' > 0$ at $p = 0$, then, λ_c and $h(\lambda_c)$ are related to the infinite volume limit. But first, let us give a heuristic argument. In the limit $\lambda \to \lambda_c$, $\lambda - gh \to 0$. By the Euler–Lagrange equation, this means $\ddot{y} \to 0$ (at $p = 0$) given $f'' \neq 0$. Since this implies that the curvature at the top vanishes, y stays at h for a longer and longer part of x leading to $V = \infty$. Note, as we have conjectured in general in the previous section.

$$h(\lambda_c) = \{2[\sigma((0,1)) + \sigma_{12}]/g\}^{1/2} = h_\infty$$

We seek a parametric form where x and y are both functions of the parameter p. Equation (4.3) can be solved easily to produce $y(p)$:

$$gy(p) = \lambda - [\lambda^2 - 2gK(p)]^{1/2} \tag{4.6a}$$

(We have kept only the physically meaningful root.) For $x(p)$, we may use $d_pK = -pf''$, $x = \int d_y x\, dy = \int d_p y\,(dp/p)$ and choose the origin ($x = 0$) to be at the right end of the crystal (Fig. 10). This yields

$$x(p) = -\int_{p_-}^{p} f''(p')[\lambda^2 - 2gK(p')]^{-1/2}\, dp' \tag{4.6b}$$

where p_- refers to the negative root of $K(p) = 0$. With this representation, it is easy to get V as a function of λ:

$$V = \int y\, dx = \int_{p_-}^{p_+} \{[1 - 2gK(p')/\lambda^2]^{-1/2} - 1\}[f''(p')/g]\, dp' \tag{4.7}$$

where p_+ refers to the positive root of $K(p) = 0$. (Of course, the second term is integrable. Although it can be related to the contact angles, we did not find this form useful.) We discuss several features of these formulas for the cases $\lambda > \lambda_c$ and $\lambda = \lambda_c$ separately.

(i) $\lambda > \lambda_c$. Since the integrands are bounded, everything is well defined; for each λ and g, one can get a unique x, y, and V. If we regard $f(p)$ as given, with λ and g as variables, then λx, λy, and $\lambda^2 V$ [or $(gy)^{1/2}$,

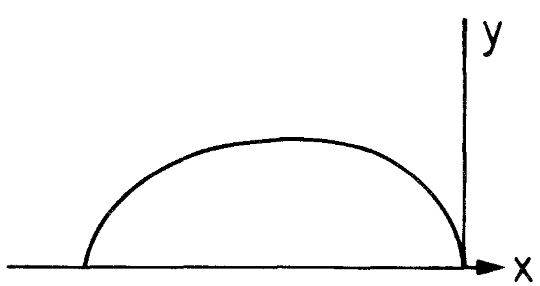


Fig. 10. The choice of origin for the x coordinate for Eq. (4.6b).

$(gx)^{1/2}$, and gV] are functions of the "scaling variable" $\xi \equiv \lambda^2/g$ alone. Using (4.6) and (4.7), one sees readily

$$\left.\frac{\partial V}{\partial \lambda}\right|_g < 0 \quad \text{and} \quad \left.\frac{\partial(x, y)}{\partial \lambda}\right|_{g,p} \leqslant 0$$

so that, by (4.4),

$$\left.\frac{\partial V}{\partial h}\right|_g > 0$$

This is to be contrasted with three dimensions where $\partial V/\partial h$ can become negative.[16,28]

(ii) $\lambda = \lambda_c$. Depending on $f(p)$, the infinite volume limit may or may not be reached as $\lambda \to \lambda_c$. The possible divergence of V (and x) rests on $(\lambda^2 - 2gK)^{1/2} = (2g)^{1/2}[K(0) - K(p)]^{1/2}$ for $\lambda = \lambda_c$. Thus, the behavior of K (and hence of f) near $p = 0$ controls the finiteness of V. From (4.7), the condition for $V(\lambda_c) = \infty$ is $\int pf''(p)/[K(0) - K(p)]^{1/2}$ diverges as $p \to 0$. If f is at least *four* times differentiable, the Taylor series for f must be $\sigma[(0, 1)] + cp^2 + O(p^3)$ with $c > 0$, for $V(\lambda_c) = \infty$, so f must be elliptic near $p = 0$.

A more interesting phenomenon occurs when (4.6), (4.7) converges for $\lambda = \lambda_c$. Then, define

$$\Sigma_{\pm} \equiv \int_0^{p_\pm} f''(p)\left[K(0) - K(p)^{-1/2}\right] dp \tag{4.8}$$

so that

$$W_{c-} \equiv x(0) = -\Sigma_-/(2g)^{1/2} \tag{4.9a}$$

$$W_{c+} \equiv x(p_+) - x(0) = \Sigma_+/(2g)^{1/2} \tag{4.9b}$$

$$V_c \equiv V(\lambda_c) \equiv \left\{f'(p_+) - f'(p_-) - \left[K(0)\right]^{1/2}(\Sigma_+ - \Sigma_-)\right\}/g \tag{4.10}$$

See Fig. 11a for a picture of $W_{c\pm}$. For $V > V_c$, the solution is made of three pieces, as in Fig. 11b, with a faceted section in the middle, of height h_c and width $W = (V - V_c)/h_c$. In both cases, $h_\infty = h_c$ although, in the latter, h_c is reached at $V = V_c < \infty$ and $dh/dV = 0$ for $V > V_c$. Finally, we point

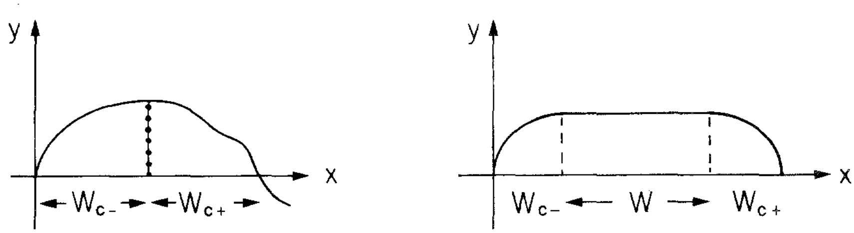


Fig. 11. Gravity-induced faceting. For small volume the crystal is as in (a) with no gravity induced facet. For larger volume there is a gravity induced facet of length W, (b).

out that, for fixed V, this gravity-induced facet appears in the latter case at the critical value

$$g_c = \{f'(p_+) - f'(p_-) - [K(0)]^{1/2}(\Sigma_+ - \Sigma_-)\}/V$$

4.2. Strictly Convex f with f' Piecewise Differentiable

Next, let us consider natural facets (i.e., facets that occur when $g = 0$) at a finite number of orientations p_α, at which points, f' is discontinuous. Now at these points, K is "undefined." However, as in the $g = 0$ case, we simply regard y as the parameter at these points and let it vary between $y(p_\alpha - 0)$ and $y(p_\alpha + 0)$. In the meantime, instead of (4.6), we use the definition $p \equiv dy/dx$ to obtain

$$x(y) = (y/p_\alpha) + \text{const.} \qquad y(p_\alpha - 0) \leqslant y \leqslant y(p_\alpha + 0) \tag{4.11}$$

(We will consider $p_\alpha = 0$ separately.) The single constant in (4.11) can be used to satisfy the boundary condition at, say, the left end of the facet. Away from these facets, (4.5) still holds while (4.6)-like formulas must be derived. Define

$$x_\alpha(p) \equiv -\int_{p_\alpha}^{p} f''(p')[\lambda^2 - 2gK(p')]^{-1/2}\,dp' \tag{4.12}$$

$$y_{\alpha\pm} \equiv y(p_\alpha \pm 0) \tag{4.13}$$

$$\Delta_\alpha \equiv y_{\alpha+} - y_{\alpha-} \tag{4.14}$$

and

$$p_0 \equiv p_-, \qquad \Delta_0 \equiv 0 \tag{4.15}$$

Then the shape is summarized by

$$x(y) = x_{\alpha-} + (y - y_{\alpha-})/p_\alpha \tag{4.16}$$

for the p_α facet and

$$\left.\begin{aligned} gy(p) &= \lambda - [\lambda^2 - 2gK(p)]^{1/2} \\ x(p) &= x_{\alpha+} + x_\alpha(p) \end{aligned}\right\} \qquad p_\alpha < p < p_{\alpha+1} \tag{4.17}$$

where

$$x_{\alpha-} = \sum_{\beta=0}^{\alpha-1} [x_\beta(p_{\beta+1}) + \Delta_\beta/p_\beta] \tag{4.18a}$$

and

$$x_{\alpha+} = x_{\alpha-} + \Delta_\alpha/p_\alpha \tag{4.18b}$$

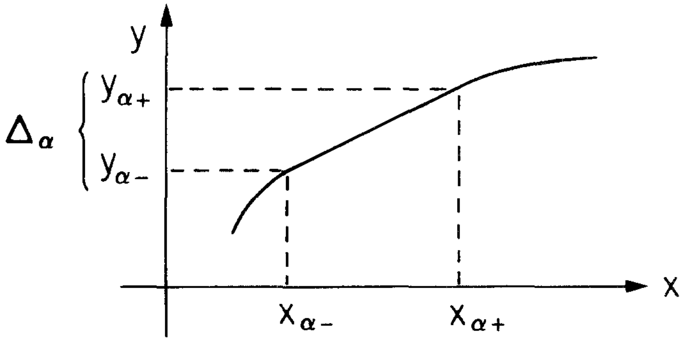


Fig. 12. The effect of gravity on facets.

A picture of the region around a facet is shown in Fig. 12.

We remark that the length of a facet (l_α) generally changes when g is applied. Using (4.2), it is easy to derive

$$l_\alpha(g,\lambda) = l_\alpha(0,\lambda)[1 - gh_\alpha/\lambda]^{-1}$$

where h_α is the height of the center of the facet (with g present) above the table.

To be complete, we need to consider the case $p_\alpha = 0$ for some α. Physically, this is the case where a natural ($g = 0$) facet is parallel to the table top. Note that pf' has no discontinuity even if f' has one. Thus, $y_{\alpha-} = y_{\alpha+}$, which indeed corresponds to a horizontal facet. The length of this facet $(x_{\alpha+} - x_{\alpha-})$ is simply $[\sigma'(0-) - \sigma'(0+)]/[\lambda^2 - 2gK(0)]^{1/2}$, which may be obtained formally from $\lim_{p_\alpha \to 0} \Delta_\alpha / p_\alpha$ or $f''(p) \to \delta(p)$ [discontinuity]. If no p_α is zero, then the possibility of gravity-induced faceting again follows the discussions in Section 4.1.

4.3. General f

To go one step further, we consider the class of f's which contain sections linear in p. As we have shown in previous sections, nonconvex f may be replaced by f^*.

Recall that, for $g = 0$, sections linear in p correspond to corners in the equilibrium shape while the orientations associated with the p's in this interval are not displayed in the shape. With the exception of the case where a corner appears at the peak (i.e., a linear section which includes the point $p = 0$), no new phenomena occur for $g > 0$. Physically, this is hardly surprising. Mathematically, equations (4.5)–(4.7) already embody these cases: $f'' = 0$ while $K = \text{const}$ for those p's in the linear section of f. Thus, both x and y remain constant as the parameter p varies through this

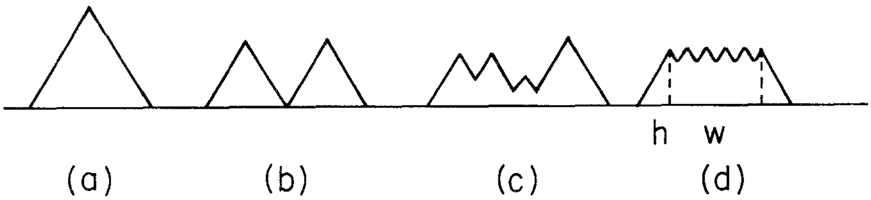


Fig. 13. Infinitesimal corrugation: A $g = 0$ pyramid, (a), will gain potential energy if g is large enough by splitting as in (b) and will further gain potential energy, without increase of surface energy, by forming the "mountain chain" in (c). The optimal shape is shown in (d) with W being flat but infinitesimally corrugated.

interval. In particular, the tangent cones to V are the same as the tangent cones to W as long as the linear section does not contain $p = 0$.

If a linear section contains the point $p = 0$, however, there is again the possibility of gravity-induced faceting, although the facet is actually an infinitesimal sawtooth. We will illustrate this phenomenon with a simple example and state the results for the general case (the proof in the next section applies to the two-dimensional case as well).

To keep the illustration simple, let us consider $\sigma_{12} = 0$, $\sigma(\hat{n}) = \sigma_0$ for $\hat{n} = \sqrt{2}\,(\pm\frac{1}{2}, \pm\frac{1}{2})$ and ∞ otherwise.[16] The $g = 0$ case is just a "pyramid" (Fig. 13a) of height $\sqrt{V}$ and base $2\sqrt{V}$.

The energy is simply $E_0 = 2\sigma_0(2V)^{1/2}$. Now, suppose $g > 0$; then the total energy for this single pyramid configuration is $E_p = E_0(1 + \tau^2/3)$, where $\tau^2 = gV/(2\sqrt{2}\,\sigma_0)$. If the shape still has only the two given normal directions, the shape could split in two (Fig. 13b) with a fixed increase in surface energy and gravitational gain proportional to g. However, Fig. (13b) is not a stable configuration: take a little square from the top of one pyramid and put it in the valley (Fig. 13c). Clearly, there's gravitational gain without increase of surface energy. The limiting form is a sawtooth-like plateau (Fig. 13d) with infinitesimal "teeth." The total energy of such a configuration is $\sqrt{2}\,\sigma_0(2h + w) + g(h^3/3 + h^2w/2)$. Minimizing this energy with respect to h and w, subject to the constraint $h(h + w) = V$, we arrive at the result $E_s = E_0(\tau^{-1} + \tau/3)$ for the total energy of the sawtooth plateau. Of course, this configuration exists only if $w > 0$, which turns out to be a condition on g, i.e.,

$$g > g_c \equiv 2\sqrt{2}\,\sigma_0/V \tag{4.19}$$

Comparing the energies associated with the single pyramid (E_p), Fig. 13a and the "mesa" with a sawtooth plateau (E_s), Fig. 13d, it is easy to see that

[16] We could equivalently use the convex integrand with this W.

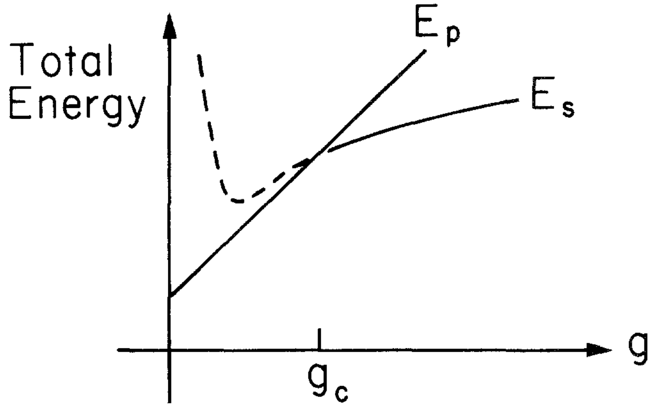


Fig. 14. g_c is the critical g where a sawtooth facet appears. There is exchange of stability between the "pyramid" and the "mesa" shapes.

$E_p > E_s$ for $g > g_c$. So, g_c is precisely the point where this type of gravity-induced facet provides a lower energy configuration (Fig. 14). τ is a dimensionless parameter indicating when the sawtooth may appear if V or σ_0 is changed instead of g.

To know that the top facets rather than curves requires ruling out infinitesimal sawteeth (varifold-type solutions if f is not convex) with tangent line slope other than $p = 0$. However, if there were such tangent lines a deformation which pushes in some high sawteeth and pushes out some lower ones (Fig. 15) would result in a configuration with approximately the same surface energy and lower gravitational energy; therefore no such tangent lines can occur. Convexity of the solutions can be shown by a similar argument.

For general f which is nonconvex in the neighborhood of $p = 0$, the critical g_c may be found in a manner similar to the previous sections. Convexify f to f^*; then $K(p) = K(0)$ for a finite interval containing $p = 0$. Thus $\int f''[K(0) - K(p)]^{1/2}\,dp$ always converge and, if there are no facets in the $g = 0$ shape, the equations (4.8)–(4.11) are still valid. If there are discontinuities in f', these equations need to be generalized as in Section 4.2.

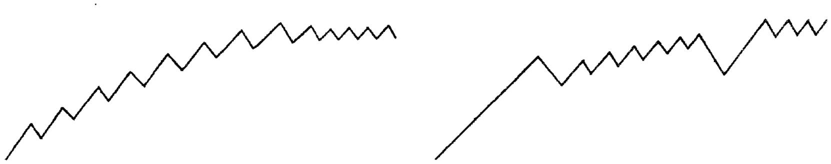


Fig. 15. Infinitesimal sawteeth are unstable for nonhorizontal directions.

5. PROOFS IN THREE DIMENSIONS

Again, we assume that f is convex and absorb $\Delta\rho$ into g.

1. Theorem. There is no gravity-induced faceting when the surface tension is elliptic.

Proof. Suppose that Ω is an open subset of R^n (for the three-dimensional case $n = 2$) and $y : \Omega \to R$ is such that the graph of y over Ω is part of the boundary of a compact solid V of prescribed volume minimizing the total energy (Fig. 16). Since the surface tension function is elliptic, the matrix $\partial_{p_i p_j}\hat{f}[\Delta y(\mathbf{x}_\perp)]$ is positive definite, where $\hat{f}$ is given in Eq. (2.9). We henceforth abbreviate $\mathbf{x}_\perp$ by x. Furthermore the boundary of V is smooth[2] and in particular y is a twice continuously differentiable function on Ω. Let $h > 0$ be the height of the crystal V so $y(x) \leqslant h$. Suppose there is a facet at height h; then $\omega = \{x \in \Omega : y(x) = h\}$ is strictly contained in Ω and contains some nonempty open subset of Ω. (Since the crystal eventually touches the table and the boundary of V is smooth, one can always choose Ω large enough so that ω is a strict subset of Ω.) The Euler–Lagrange equation

$$\sum_{i,j=1}^{n} \partial_{p_i p_j}\hat{f}\left[\nabla y(x)\right]\partial_{x_i x_j} y(x) = g y(x) - \lambda$$

implies $h = \lambda/g$ [this follows from Eq. (2.7b) since a facet on top gives $K_{1,2} = 0$]. If we write

$$a^{ij}(x) = \partial_{p_i p_j}\hat{f}\left[\nabla y(x)\right], \qquad i, j = 1, \ldots, n$$

$$u(x) = y(x) - h$$

then the Euler–Lagrange equation becomes

$$\sum_{i,j=1}^{n} a^{ij}(x)\partial_{x_i x_j} u(x) - g u(x) = 0$$

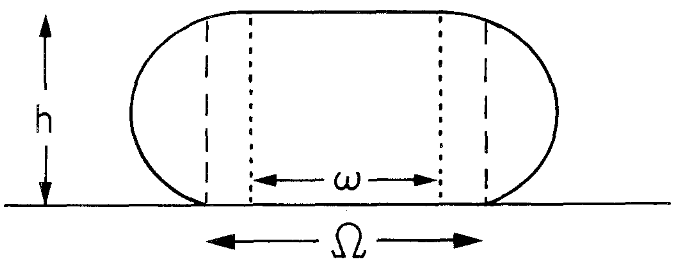


Fig. 16. The construction used in proving 1. ω is the putative gravity-induced facet. h is the height of the crystal.

Since the matrix $[a^{ij}(x)]_{ij}$ is positive definite and $g \geqslant 0$, we infer from the strong maximum principle of E. Hopf[19] that u cannot achieve a nonnegative maximum in Ω unless u is constant. Therefore $u(x) = 0$ for each x in Ω; hence $y(x) = h$ for each x in Ω. This contradicts the fact that ω does not equal Ω. ■

2. Proposition. Suppose that V is a solid of prescribed volume which gives a local minimum for the total energy E and that W (the $g = 0$ shape) is a polyhedron. Suppose that $\hat{n} \neq \hat{z}$ has the property that either σ is smooth at $\hat{n}$ (so that $\hat{n}$ is one of an open set of unit vectors corresponding to a corner of W) or σ has a crease at $\hat{n}$ which is perpendicular to some horizontal vector (so that $\hat{n}$ is one of a one-dimensional family of unit vectors corresponding to a horizontal edge of W). Then, in the first case, $\hat{n}$ is not normal to V, and in the second case $\hat{n}$ is not normal to V if V is a convex polyhedron.

Proof. Suppose that V has normal $\hat{n}$ at point $\mathbf{x}$, where $\hat{n}$ corresponds to a corner of W. Deform V in a neighborhood of $\mathbf{x}$ by pushing V out so that it looks like the corner of W corresponding to $\hat{n}$; let ΔV be the change in volume (Fig. 17).

The change in surface energy due to this deformation is precisely zero if the boundary of V is planar near x; otherwise it is zero to first order in ΔV.[41] The change in gravitational energy is $g \Delta V z_0$ where $z_0 = \mathbf{x} \cdot \hat{z}$. Now rescale this deformed V back to the original volume, by the scale factor $s = [V/(V + \Delta V)]^{1/3}$. As usual, the total change in energy, assuming V is at equilibrium, is, to first order in ΔV

$$0 = \Delta E = \Delta V(-\lambda + g z_0)$$

But $\hat{n} \neq \hat{z}$ implies that $z_0 < h$ and hence $-\lambda + g z_0 < 0$, a contradiction.

In the second case, there exists $\hat{n}_1$ and $\hat{n}_2$, normals to adjacent faces of W, such that $\hat{n} = a_1 \hat{n}_1 + a_2 \hat{n}_2$ for some positive a_1, a_2. Suppose V is convex and a polyhedron. The boundary of V near $\mathbf{x}$ must look like Fig. 18; that is, it is a ruled surface (with horizontal rulings), breaking off at the ends of the

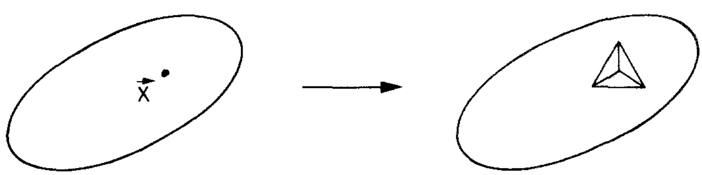


Fig. 17. The construction used in proving 2. Directions which are absent in the $g = 0$ shape are absent by an instability argument also when $g \neq 0$.

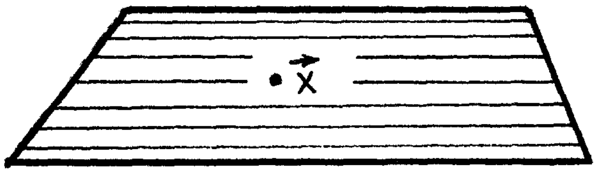


Fig. 18. The ruled surface used in the proof of 2.

rulings to other plane segments. We may restrict this part of the boundary of V to be a quadrilateral. For small enough ϵ and $0 < \delta \ll \epsilon$, we deform V as indicated in Fig. 19, making a horizontal furrow of depth δ at height $z_0 = \mathbf{x}_0 \cdot \hat{z}$ and a horizontal ridge of height δ at height $z_0 - \epsilon$; the normals to the sides of the furrow and ridge are $\hat{n}_1$ and $\hat{n}_2$.

Since $\sigma(\hat{n}) = a_1\sigma(\hat{n}_1) + a_2\sigma(\hat{n}_2)$,[41] the only change in surface energy due to this deformation is from what happens at the ends of the ridge and furrow; since the same areas are cut out for the furrow as are added to the ridge (and in the same plane segments), the change in surface energy is zero (in the curvilinear case, this is not true, and this reasoning fails). The volume cut out to make the furrow is of order $\delta^2 l_1 c_0$, where c_0 is some positive constant and l_1 is the length of the furrow. The volume added to make the ridge is (to order δ^2) $\delta^2 l_2 c_0$, where l_2 is the length of the ridge, leading a net volume change of $\Delta V \approx \delta^2 c_0(l_2 - l_1)$. The gravitational energy change is $gz_0\Delta V - \epsilon\delta^2 l_2 c_0$. Again, we rescale and deform V back to the original volume, obtaining the energy change

$$\Delta E = \Delta V(-\lambda + gz_0) - \epsilon g\delta^2 l_2 c_0$$

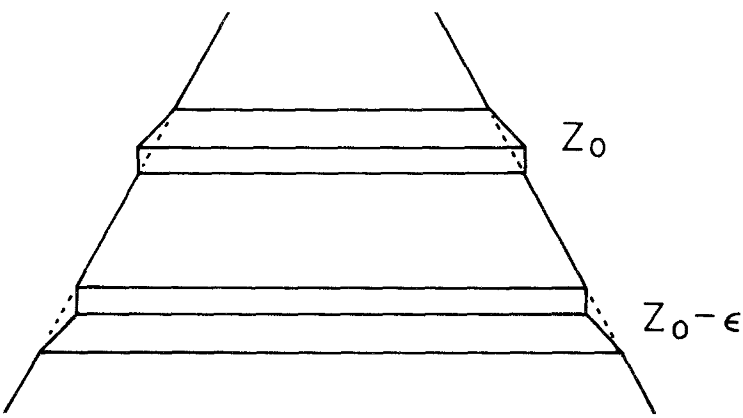


Fig. 19. A ridge and a furrow which lower the energy of the putative surface.

If $l_2 - l_1 \geqslant 0$, then $\Delta V \geqslant 0$ and hence $\Delta E < 0$, a contradiction. If $l_2 - l_1 < 0$, then one can run this deformation in the opposite direction, making a ridge at height z_0 and a furrow at height $z_0 - \epsilon$. One obtains $\Delta E = O(\delta^2)$, $\Delta V < 0$, and

$$0 = \Delta V\left[-\lambda + gz_0 + \epsilon l_2/(l_1 - l_2)\right]$$

But $\epsilon/(l_1 - l_2)$ is constant as a function of ϵ, and l_2 varies (since $l_2 \neq l_1$). This is a contradiction. ■

3. Theorem. There is gravity induced faceting or curvature if W is polyhedral and V is convex. That is, suppose that $V = V_g$ is a solid of prescribed volume which minimizes E_g (the total energy with gravitational constant g), and suppose that V_g is convex. Suppose further that W (i.e., the $g = 0$ crystal) is a polyhedron which does not have $\hat{z}$ as a normal. Then if g is large enough, V has a facet or is curved on top; in case W has an edge on top, suppose further that V is not curved on top.

Proof. Suppose that V is convex and has no facet on top; in case W has an edge on top, suppose further that V is not curved on top. We will show that for large enough g, this contradicts the minimality of V.

Let h be the maximum height of V, and let $m =$ dimension $\{x \in V: \hat{z} \cdot x = h\}$. If $m = 0$, there is a corner in V pointing up; if $m = 1$, there is a horizontal line segment L of length $l > 0$ on top of V. By assumption $m \leqslant 1$.

Since V_g is at equilibrium, $\lambda - gh \geqslant 0$, and therefore (from the virial theorem $\lambda \leqslant \text{const}\, g^{1/2}$), h must go to zero as g goes to infinity. By the convexity of V_g, and the fact that all directions near $\hat{z}$ do not occur as normals to V_g,

$$\text{const}\, h^3 \geqslant \text{volume}(V_g), \qquad \text{if} \quad m = 0$$

$$\text{const}\, h^3 + \text{const}\, h^2 l \geqslant \text{volume}(V_g), \qquad \text{if} \quad m = 1$$

Thus we have an immediate contradiction in the case $m = 0$, since the volume is fixed.

In case $m = 1$, we examine the pillbox comparison surface more closely. Letting h_c be its height, the gravitational energy is $gVh_c/2$ and the surface energy is no more than $[\sigma(\hat{z}) + \sigma_{12}]V/h_c + 4(V/h_c)^{1/2}h_c \max\sigma$. Choosing $h_c = [2(\sigma(\hat{z}) + \sigma_{12})/g]^{1/2}$, which is the value which minimizes the total energy of such a pillbox, ignoring the lower terms, we obtain $E_c = V[2g(\sigma(\hat{z}) + \sigma_{12})]^{1/2}\{1 + O(1/g)\}$. Since the pillbox is a comparison shape, $E \leqslant E_c$. Note that

$$\lambda = (2E_s + 4E_G)/3V < 4E/3V \leqslant (4/3)\left[2(\sigma(\hat{z}) + \sigma_{12})g\right]^{1/2}$$

since h is the maximum height of V, then $\lambda - gh \geqslant 0$ and we have

$$h \leqslant \lambda/g < (4/3)\{2[\sigma(\hat{z}) + \sigma_{12}]/g\}^{1/2} = (4/3)h_c$$

Assume the ridge in V runs parallel to the y axis from $y = 0$ to $y = l$. Let $w(y)$ be the maximum width of the cross section of V at y. Let $a = (\min \sigma)/[\sigma(\hat{z}) + \sigma_{12}]$, and let α be such that h would equal αw if the cross section of V were a triangle (and the normals to the sides of V were $\hat{n}_1$ and $\hat{n}_2$, the normals to W on either side of the top ridge). Let $h_0(y) = h - \alpha w(y)$. Proposition 2 implies $h_0(y) \geqslant 0$, since V is convex and noncurved.

We have

$$E_S \geqslant \left[\sigma(\hat{z}) + \sigma_{12}\right]\int_0^l (w + ah_0)\, dy$$

since $V < h\int_0^l w\, dy$, and since

$$E_S \leqslant E_c = 2\left[\sigma(\hat{z}) + \sigma_{12}\right]V/h_c$$

we have $h \geqslant h_c[1 + ah_0/w]/2$.

If $h_0 \leqslant h_c/4$, then (since in particular $h \geqslant h_c/2$), we have $w \geqslant h_c/4\alpha$. Otherwise,

$$h = h_0 + \alpha w \geqslant h_c a h_0/w \geqslant (3/2)a\alpha h_0^2$$

(since $h_0 < h \leqslant (4/3)h_c$); solving this inequality for w one obtains

$$w \geqslant -h_0 + h_0\left[1 + (3/2)\alpha a\right]^{1/2} \geqslant \left[(1 + (3/2)\alpha a)^{1/2} - 1\right]h_c/4$$

Thus w is always at least a fixed fraction of h_c. Since $(4/3)h_c \geqslant w + h_0$, w is also at least a fixed fraction of h.

Finally, this implies that there is a deformation which flattens V, keeps w the same, and reduces the height of the center of gravity of each slice by at least a fixed fraction of w, and hence of h and h_c. Therefore this deformation decreases E by an amount proportional to $E \leqslant E_c$. This contradicts the fact that E is assumed to be the minimum value of the total energy (and justifies the neglect of the lower-order terms in the energy). ■

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NOTE ADDED IN PROOF

After completing this paper, the authors received a preprint from C. Rottman and M. Wortis entitled "Statistical Mechanics of Equilibrium Crystal Shapes: Interfacial Phase Diagrams and Phase Transitions" which deals with gravity-free cases. Also, gravity-induced curvature rather than gravity-induced facetting seems to be the rule when W is a polyhedron with an edge on top, according to current research by J.E.T.

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