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Alternative to the Shuttleworth formulation of solid surface stress

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We examine two derivations of the Shuttleworth equation (which is a relation between surface stress g, surface tension γ, and surface strain), and identify the flaws we perceive. Rectifying the perceived flaws leads not to the Shuttleworth equation but to g-γ equivalence. We conclude that surface stress is merely the generalization of the concept of surface tension to an elastically anisotropic system; the surface free-energy density is one-half of the trace of the surface stress tensor, to lowest order. In our opinion, our conclusions lead to a more coherent and elegant form of surface thermodynamics which should prove useful in controlling and in understanding nanometer-scale fabrication.

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A key component of future technology is expected to be devices fabricated on the nanometer scale. The previous decade was one in which this idea motivated a great deal of research into the behavior of and fabrication of condensed-matter structures on the nanometer scale. For example, carbon nanotubes—hollow cylinders made of carbon atoms—were fabricated,[1] GaAs and Ge nanowires were grown epitaxially,[2,3] and quantum dots—three-dimensional islands, most notably of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ on GaAs surfaces—were investigated for their promising optoelectronic properties.[4,5]

The influence of surfaces and interfaces on device properties will increase as the device size decreases. A property common to many of the nanoscale systems is the presence of facets on the surfaces of the nanostructures. For example, $\{133\}B$ facets bound the surfaces of GaAs nanowires grown on GaAs(113)A (Ref. 2); $\{159\}$ facets bound the surfaces of Ge nanowires grown on Si(113) (Ref. 3); and the surfaces of InAs dots grown on GaAs(001) are bounded by $\{113\}A$ and $\{136\}A$ facets.[6,7] The presence of facets makes it clear that one must use surface thermodynamics in order to understand the origin of the nanostructure shape. The equilibrium crystal shape in the absence of external stress is given by minimizing the integral

$$f^{\mathrm{surf}}=\int \gamma(A)dA, \tag{1}$$

where f^{surf} is the surface free energy, γ is the surface tension, and the integral is taken over the entire surface area A.[8,9]

Aside from Eq. (1), it is generally thought that the most important equation in the domain of the equilibrium shapes of surfaces is the Shuttleworth equation, given by

$$g_{ij}=\gamma\delta_{ij}+\left[\frac{\partial\gamma}{\partial e_{ij}}\right]_T \tag{2}$$

where g_{ij}, e_{ij}, and δ_{ij} are the surface stress tensor, the surface strain tensor, and the Kronecker delta, respectively, and the partial derivative is evaluated at a constant temperature T.[9] This equation (or rather a more primitive version of it) was first derived by Shuttleworth in 1950, and is understood to define the relation between surface stress, surface tension, and surface strain.[10] It is the goal of this paper to show that Eq. (2) is not the only possible relation between these quantities: an alternative relation exists which, in our opinion, leads to a more useful, coherent, and elegant form of surface thermodynamics.

In the year 2000, Sanfeld and Steinchen calculated the surface energy, surface stress, capillary-elastic pressure, and chemical equilibrium constant in nanoparticles.[11] In the introduction to their paper, Sanfeld and Steinchen noted that the distinction between surface energy, surface tension, and surface stress is still a cause of controversy. For example, they stated that the interpretation of compressive and tensile surface stress contributions remains controversial. Sanfeld and Steinchen gave the perfectly reasonable view that these controversies arise from insufficiently rigorous distinctions between the various terms. We tend to agree with this view, but we would go further. We think that the existence of such a controversy half a century after Shuttleworth's original paper is evidence that there could be something seriously amiss with the Shuttleworth equation itself.

We will begin by reviewing some elements of surface thermodynamics theory, principally following Zangwill.[9] Including the surface, the differential of the internal energy U is given by

$$dU=T\,dS-P\,dV+\mu\,dN+\gamma\,dA, \tag{3}$$

where S, P, V, μ, and N are the entropy, pressure, volume, chemical potential, and number of atoms, respectively.[12] One has also the Euler equation[9]

$$U=TS-PV+\mu N+\gamma A. \tag{4}$$

Differentiating Eq. (4) and applying Eq. (3), one obtains the Gibbs-Duhem equation

$$A\,d\gamma+S\,dT-V\,dP+N\,d\mu=0. \tag{5}$$

If we consider the surface free energy f^{surf} in isolation, by Eqs. (3) and (4) one has

$$f^{\mathrm{surf}}=\gamma A, \tag{6a}$$

$$df^{\mathrm{surf}}=\gamma\,dA. \tag{6b}$$

Now let us consider the derivation of Eq. (2), but simplified to the case of uniaxial surface stress on a flat surface, in order to clarify the physics involved, as in the work of Pimpinelli and Villain.[13] Let the direction of uniaxial surface stress be the *x* direction, which results in a surface stress g_{xx} and a surface strain e_{xx}. For f^{surf}, Pimpinelli and Villain wrote

$$f^{\mathrm{surf}}=A\gamma(e_{xx})=(A_0+\delta A)(\gamma_0+\delta\gamma)$$
$$=(A_0+\delta A)\left(\gamma_0+\frac{\partial\gamma}{\partial e_{xx}}e_{xx}\right), \tag{7}$$

where the zero subscript denotes the parameter value in its initial state, and the delta terms refer to the change in a given parameter between the initial and final states. Using $\delta A=A_0e_{xx}$ one therefore has

$$\delta f^{\mathrm{surf}}=\gamma_0\delta A+A_0\delta\gamma=\delta A\left(\gamma_0+\frac{\partial\gamma}{\partial e_{xx}}\right). \tag{8}$$

Note that the non-numbered equation before Eq. (16.35) of Pimpinelli and Villain has a superfluous e_{xx}.[13] One may obtain the change in f^{surf} due to reversible work, $-$PdV, using the analogous term for the surface, i.e., from the mathematical transformation $V\rightarrow A$ and $-P\rightarrow g_{xx}$. This gives

$$\delta f^{\mathrm{surf}}=g_{xx}\delta A, \tag{9}$$

and hence Eqs. (8) and (9) give the result for the *xx* tensor element of Eq. (2). (Here *P* and g_{xx} are taken to be opposite in sign because a compressive *P* is positive whereas a compressive g_{xx} is negative). Similar arguments lead to the other tensor elements of Eq. (2).

What objections can one raise to the above derivation of the Shuttleworth equation? If we differentiate Eq. (6a), we obtain

$$df^{\mathrm{surf}}=\gamma\ dA+A\ d\gamma. \tag{10}$$

But by Eq. (6b) we have

$$A\ d\gamma=0, \tag{11}$$

which is, incidentally, what remains of Eq. (5) if we drop the variables *S*, *T*, *V*, *P*, μ, and *N*, e.g., if we ignore bulk effects. Equation (11) implies that the term $A_0\delta\gamma$ in Eq. (8) vanishes, even though the expansions in Eqs. (7) and (8) appear to imply that $A_0\delta\gamma$ does not necessarily vanish. Logically, this contradiction can be eliminated only by assuming that γ cannot be changed in this system, i.e., that $\delta\gamma$ is zero. Use of the state function f^{surf} in isolation (i.e., ignoring the variables *S*, *T*, *V*, *P*, μ, and *N*) is therefore restricted to systems at constant γ, by Eq. (11): the expansions in nonzero $\delta\gamma$ in Eqs. (7) and (8) are forbidden because they violate an axiom in the mathematical structure. If we compare Eqs. (6b) and (9), we simply have the result that surface stress and surface tension are identical in the isotropic limit: the Shuttleworth equation does not follow. We will call this result ‘‘*g*-γ equivalence,’’ where *g* is isotropic surface stress. The wider implication of this result is that the surface stress is the generalization of the concept of surface tension to anisotropic systems, since the surface stress is a second-rank tensor whereas the surface tension is a scalar.

Another problem with the above derivation of the Shuttleworth equation is that Eq. (11) does not follow automatically for all systems from the more general Eq. (5). Equation (11) arises only if f^{surf} is considered in isolation from *U*. While it is an acceptable approximation in many circumstances to neglect surface effects in bulk thermodynamics, it is not permissible to neglect bulk effects universally when calculating surface thermodynamic phenomena. For example, in the above derivation, in order to obtain a surface stress g_{xx} by external mechanical perturbation it is necessary to change the bulk stress tensor element σ_{xx}, which will in turn alter *U* and hence will influence some terms in Eq. (5). Since the above calculation treats f^{surf} in isolation from *U*, the derivation of Eq. (2) does not follow, because such a treatment leads to Eq. (11) which then forbids variation in γ.

A further criticism of the above Shuttleworth equation derivation is that the differential *dA* (or δA) is not used in the standard sense. In Eqs. (3) and (6b), *dA* is a surface area element to be integrated over in order to generate the whole surface area, whereas δA in Eq. (9) was taken in Ref. 13 to be the additional area generated through the action of surface stress. These senses are mutually inconsistent. If the interpretation is made consistent i.e., that *dA* (or δA) is a surface area element, the above *g*-γ equivalence follows. We will return to this point later.

Zangwill gave a derivation of the Shuttleworth equation which differed from the derivation in Pimpinelli and Villain in that the terms *S*, *T*, *V*, *P*, μ, and *N* are included[9,13]. Here we show that Zangwill's derivation results from contradictory assumptions—when the contradiction is eliminated, the Shuttleworth equation does not follow. Zangwill obtained

$$dU=T\ dS-P\ dV+\mu\ dN+Ag_{ij}\ de_{ij}, \tag{12}$$

as the second equation of Zangwill's Eq. (1.9). [To avoid confusion, we state that Zangwill's Eq. (1.9) contains a superfluous *A* in the final term.] Zangwill then used Euler's equation adapted to include surface effects in the isotropic limit, namely, Eq. (4). The γA term in Eq. (4) only addresses isotropic cases because γ is a scalar.[14] By contrast g_{ij} and e_{ij} in Eq. (12) are second-rank tensors, which can describe anisotropic cases up to C_{2v} in symmetry, by Neumann's principle.[14] If one uses Eqs. (4) and (12) simultaneously, one must restrict the results to isotropic surface systems (here taken to imply C_3 symmetry or higher), to avoid contradiction. Differentiating Eq. (4) and applying Eq. (12), Zangwill obtained

$$A\ d\gamma-S\ dT+V\ dP-N\ d\mu+A(\gamma\delta_{ij}-g_{ij})de_{ij}=0. \tag{13}$$

For isotropic surface systems, g_{ij} can be written as $g\delta_{ij}$, where *g* is a scalar. Likewise, de_{ij} can be written as $\delta_{ij}de$, where *e* is a scalar. Hence

$$A(\gamma\delta_{ij}-g_{ij})de_{ij}=2A(\gamma-g)de, \tag{14}$$

since $\delta_{ij}\delta_{ij}=2$ for the surface. Zangwill stated that $dA/A=de_{ij}\delta_{ij}$: from this equation we obtain

$$dA=A\ de_{ij}\delta_{ij}=2A\ de, \tag{15}$$

taking the isotropic limit. Combining Eqs. (13)–(15), the result is

$$A\ d\gamma - S\ dT + V\ dP - N\ d\mu + (\gamma - g)dA = 0. \tag{16}$$

This is evidently the Gibbs-Duhem equation for a system (liquid or solid) with an isotropic surface. For isotropic surface systems, γ and A are thermodynamically conjugate variables. Hence one of the terms containing dA or $d\gamma$ in Eq. (16) is zero, as required by the contact manifold mathematical structure of equilibrium thermodynamics.[15] [Mathematically, this is the reason for the absence of the $T\,dS$, $-P\ dV$, and $\mu\ dN$ terms from Eq. (16), because their respective complementary terms $-S\ dT$, $V\ dP$, and $-N\ d\mu$ are present.] If $A\ d\gamma$ were zero, this would imply a zero surface area A in general, or the inability to vary γ, both of which are unphysical. [In Eq. (16), $A\ d\gamma = 0$ is not implied by Eq. (11), because Eq. (11) is derived assuming one can ignore the variables S, T, P, V, μ, and N in Eq. (16).] Therefore the $(\gamma - g)dA$ term is zero: γ and g are equal. The result leads to the Gibbs adsorption equation originally derived by Gibbs,[16] i.e., without the final term in Zangwill's Eq. (1.11). Without the final term, the Shuttleworth equation does not follow. Our earlier result of g-γ equivalence is confirmed in a more rigorous fashion.

For anisotropic surface systems, we replace γA in Eq. (4) with $Ag_{ij}\delta_{ij}/2$. This substitution is made using our insight that γ and g are identical in isotropic systems. Two equations which follow from this substitution are

$$dU = T\ dS - P\ dV + \mu\ dN + g_{ij}\delta_{ij}\ dA/2, \tag{17}$$

$$A\delta_{ij}\ dg_{ij}/2 - S\ dT + V\ dP - N\ d\mu = 0, \tag{18}$$

where Eq. (17) supercedes Eq. (12), and Eq. (18) is the Gibbs-Duhem equation for anisotropic surface systems. Gibbs's original adsorption equation then follows, except that the $A\ d\gamma$ term is replaced by $A\delta_{ij}\ dg_{ij}/2$. [The off-diagonal element of g_{ij} gives second-order contributions to f^{surf}, through a higher-order term $g_{ij}e_{ij}/2$ within the brackets in Eq. (21) below; $g_{ij}e_{ij}/2$ is typically negligible in Eq. (21) within the linear elastic regime.]

We wish to make a remark regarding the use of the dA term by Zangwill.[9] In that work, dA is used in two different senses. In one sense it is a surface area element, which is to be integrated to cover the whole surface, as in Zangwill's Eq. (1.19). In the other sense it is an infinitesimal change in the surface area due to the action of surface stress, as with the equation $dA/A = de_{ij}\delta_{ij}$ of Zangwill mentioned above. Only in the latter case, therefore, does dA correspond to infinitesimal surface strain. Here we have followed the ambiguous usage, because it would be difficult to discuss the work in Refs. 9 and 13 otherwise. We favor using dA strictly as a surface area element to be integrated in order to cover the whole surface, as in Eqs. (1), (3), and (21) below.

In the formal context of our derivation of g-γ equivalence, note that in its construction we made no *a priori* assumption about the equality, or otherwise, of g and γ. The Shuttleworth equation leads to $g \neq \gamma$ for solid surfaces. The *a priori* hypothesis that $g \neq \gamma$ is incompatible with our formulation: for self-consistency our formulation of solid surface stress requires g-γ equivalence to be true.

Let us consider how surface thermodynamics develops from the point of view of g-γ equivalence. First let us consider Hooke's law for the surface,

$$g_{ij} = c^{\mathrm{surf}}_{ijkl} e_{kl}, \tag{19}$$

where a repeated index implies summation (from 1 to 2) with respect to orthonormal basis vectors in the surface plane, and c^{surf}_{ijkl} are the elements of the surface stiffness tensor.[17] In fact, we do not know *a priori* that a typical surface will be in the linear elastic regime (to which Hooke's law applies), but support for this assumption is given below.

We will remark now that from comparing Eqs. (2) and (19), the $(\partial\gamma/\partial e)_T$ term in the Shuttleworth equation for a solid surface has a property which we find to be incoherent. As stated by Hirth, $(\partial\gamma/\partial e)_T$ is approximately equal to $-\gamma\delta_{ij}$ for a solid surface, the difference between these quantities being $c^{\mathrm{surf}}_{ijkl}e_{kl}$.[17] If we consider the simple case of a surface with isotropic surface stress such as Si(111), and bear in mind that γ is the tensile force in the surface plane perpendicular to any straight unit length in the surface, we think it questionable that the rate of change of γ with respect to small surface strains (e.g., 1%) should be approximately equal to $-\gamma$. It is this property of Eq. (2) which led us to examine its derivation in detail.

The general form of g_{ij} on a C_1 symmetry surface is

$$g_{ij} = \begin{pmatrix} g_{11} & g_{12} \\ g_{12} & g_{22} \end{pmatrix}, \tag{20}$$

where the two axes are orthonormal and in the surface plane, which is under zero stress by external sources.[17] For surfaces of C_{1v} or C_{2v} symmetry, with the second axis perpendicular to a mirror plane, Eq. (20) is simplified by g_{12} being zero. For C_3 symmetry surfaces or higher, Eq. (20) is further simplified by g_{11} and g_{22} being equal: one can write $g_{ij} = \gamma\delta_{ij}$ for a g-γ equivalent f^{surf}, as for a liquid surface. To summarize, to lowest order the surface free energy is given by

$$f^{\mathrm{surf}} = \int \left(\frac{\delta_{ij} g_{ij}(A)}{2} \right) dA. \tag{21}$$

The integral in Eq. (21) is taken over all the surfaces and interfaces in the system. (Note that, for the surface, $\delta_{ij}\delta_{ij} = 2$.) Equation (21) implies that the surface free-energy density is given by half of the trace of the surface stress tensor, to first order. One can call this quantity $\overline{\gamma}$, the mean surface tension, since it is equal to $(g_{11} + g_{22})/2$. Equation (1) is recovered from Eq. (21) in the isotropic limit, to lowest order.

One might object to the application of Hooke's law to a liquid surface for a g-γ equivalent f^{surf}, since Eq. (19) implies that $(\partial\gamma/\partial e)_T$ is nonzero for the liquid surface. Here both diagonal elements of the surface stress tensor (g_{11} and g_{22}) and the surface tension are taken to be equal; e is the isotropic surface strain. It is clear that a low viscosity liquid cannot be put under surface strain by an external mechanical perturbation.[9] A simple illustration of this effect is to try to pull apart the surface of some water with one's hands. No change in the water's surface strain is accomplished. The effect would not occur if the water were replaced by a sufficiently hard material.

However, this does not disprove the validity of Hooke's law for the liquid surface. The liquid surface must possess an intrinsic surface strain. For liquids and solids, the surface is like an elastic skin which is stretched over the bulk: if one could remove the bulk from the interior, the surface would shrink to a smaller size. (One way to visualize this process is to consider a hand entering and stretching a tight-fitting rubber glove, where the hand represents the bulk and the rubber glove represents the surface.) The surface tension of the liquid is the static force perpendicular to unit length on the surface, where the force is that stretching the surface in order that it fit over the bulk. The surface has an intrinsic surface strain, because it is under tension through being stretched by the bulk. On the basis of Hooke's law for the surface [Eq. (19)]—the linear relation between surface stress and surface strain—it follows that $(\partial\gamma/\partial e)_T$ is nonzero for the liquid surface, since $(\partial\gamma/\partial e)_T$ is equivalent to an elastic constant. $(\partial\gamma/\partial e)_T$ is therefore nonzero, even though changing γ or e for a liquid surface in experiment through mechanical perturbation appears to be impossible. The liquid surface has a nonzero surface strain even if the surface is in the nonlinear elastic regime, i.e., if the surface stress is some second-order or higher-order polynomial function of surface strain.

For g-γ equivalence, Eq. (2) does not apply and the equation of surface linear elasticity is Eq. (19). We will consider the case of the macroscopic C_{4v} symmetry Si(001) surface for illustrative purposes, for which we take γ to be 1.36 $\mathrm{J\,m^{-2}}$.[18] We do not know of any reports of the surface elastic constants of Si(001), so we will estimate them by taking the surface to be of bilayer thickness t_B and using

$$c_{ij}^{\mathrm{surf}}=c_{ij}t_B, \tag{22}$$

where the contracted tensor element notation is used, and c_{ij} are bulk elastic stiffness constants.[14] For Si(001), we obtain c_{11}^{surf} and c_{12}^{surf} values of 45.0 and 17.3 $\mathrm{J\,m^{-2}}$, respectively.[19] By Eqs. (19) and (20),

$$g_{11}=(c_{11}^{\mathrm{surf}}+c_{12}^{\mathrm{surf}})e_{11}=\gamma, \tag{23}$$

and we obtain $e_{ij}=+2.2\%\,\delta_{ij}$. A surface strain of 2.2% is one for which we can expect linear elasticity theory to apply, which supports our earlier assumption of the linear elastic regime. In the case of heteroepitaxy, the surface stress arising from heteroepitaxy should be added to that present in the absence of heteroepitaxial stress to yield the total surface stress. By the principle of superposition, for a flat, nonrelaxed heteroepitaxial film, one can write

$$g_{ij}=g_{ij}^{I}+g_{ij}^{H}, \tag{24}$$

$$e_{ij}=e_{ij}^{I}+e_{ij}^{H} \tag{25}$$

for the total surface stress and total surface strain, respectively, where the I and H superscripts denote the parts which are intrinsic to the surface, and which arise from heteroepitaxy, respectively. (This neglects effects due to the finite thickness of the film, discussed recently by Müller and Thomas[20]). In the g-γ equivalent formalism, no part (total, intrinsic, or heteroepitaxial) of the surface stresses or surface strains obeys a relation similar to the Shuttleworth equation. By way of example, for Ge on a Si surface $e_{ij}^{H}=-3.8\%\,\delta_{ij}$, which is opposite in sign to the intrinsic surface strain.[19] By Eqs. (19), (21), and (25), this will lead to a negative surface energy, which could act to stabilize the flat film during the earliest part of growth in the Ge on the Si Stranski-Krastanow growth mode. (Normally, a negative surface energy is taken to imply $A\rightarrow\infty$, i.e., instability, but here an increasing A might not be favored because it will lead to strain relaxation, which will increase the total surface strain in Eq. (25) and hence this might increase f^{surf}.) Müller and Kern noted that at present it is difficult to treat the Stranski-Krastanow growth mode theoretically in a satisfactory manner.[21] In general, one expects nanostructure shapes to arise by minimizing the surface and bulk stress energies in concert, within the bounds of the equilibrium states to which the system has access.

We should make clear the extent of the approximations inherent to Eq. (22). Because of the similarity in the bonding parallel to the surface plane, we take the c_{ij} to be fairly constant as one approaches the surface from the bulk. The units of the c_{ij} and c_{ij}^{surf} are different: one has to multiply the c_{ij} by the thickness characteristic of the surface in order to obtain the c_{ij}^{surf}. Due to the approximations present, we have considered only the elastic constants of isotropic bulk and surface systems. We have taken the representative thickness of the surface to be t_B which we expect to be accurate to within a factor of 2. For a pessimistic assessment of surface strain, namely, taking the surface to be of monolayer thickness, and assuming that Eq. (22) overestimates the c_{ij}^{surf} by 50%, one obtains a surface strain of +6.6%, which approaches the regime in which the linear elastic approximation ceases to be valid. The choice of surface elastic constants and surface strain is therefore fairly arbitrary in this macroscopic theory: what is not arbitrary is that, when these two quantities are combined [Eq. (19)], one must obtain a surface stress tensor (for isotropic surface stress, a surface tension) which is in agreement with values derived from experiment. We emphasize that the numerical accuracy of the example of the Si(001) surface given for illustrative purposes has no bearing on the validity of exploring the consequences of g-γ equivalence.

We will examine the possibility that the surface strain has a drastic influence on the surface elastic constant expression $c_{11}^{\mathrm{surf}}+c_{12}^{\mathrm{surf}}$, which occurs within Eq. (23). If we consider the effect of a hydrostatic strain of +2.2% (equal to the surface strain calculated above) on Si this will decrease the corresponding bulk elastic constant expression $c_{11}+c_{12}$ by 24%. This result is calculated using the dependence of the c_{ij} of Si on pressure measured in Ref. 22. The result is an upper limit on the change in $c_{11}^{\mathrm{surf}}+c_{12}^{\mathrm{surf}}$ because the surface is two dimensional, thereby permitting some elastic relaxation in the direction perpendicular to the surface. In the context of the other approximations present in the calculation of the surface strain, therefore, it is permissible to take the c_{ij}^{surf} as being independent of surface strain. Given the 24% change in $c_{11}+c_{12}$ calculated above (which means that the average value of $c_{11}+c_{12}$ during the process of changing the strain from zero to $+2.2\%$ is 12% lower than the value at zero strain), it would be wise to quote the Si(001) surface strain as being between $+2.2\%$ and $+2.5\%$ in the limit of the bilayer-thick surface model.

In this paper we have examined two derivations of the Shuttleworth equation, and have identified the flaws we perceive. Rectifying the perceived flaws leads not to the Shuttleworth equation but to g-γ equivalence. In the g-γ equivalent formalism, surface stress is merely the generalization of the concept of surface tension to an elastically anisotropic system; the surface free-energy density is given by one-half of the trace of the surface stress tensor, to lowest order. After making some assumptions, we obtain a tensile surface strain of 2.2% for the Si(001) surface, which supports the assumption that this surface is in the linear elastic regime. We hope that the g-γ equivalent formalism will prove useful in controlling and in understanding nanoscale fabrication.

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