Non-Equilibrium Continuum Physics **TA session #7**

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Perturbative expansion and linear stability analysis

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1 Perturbative expansion: the Asaro–Tiller–Grinfeld (ATG) instability

We first examine the Asaro–Tiller–Grinfeld (ATG) instability, to demonstrate how linear elasticity combined with additional physics yields non-trivial spatiotemporal instabilities.

The ATG instability deals with the behavior of a solid submitted to uniaxial stress while in contact with its melt (i.e. solid-liquid interface). We will be following "Directional solidification under stress" by I. Cantat *et. al.*, Phys. Rev. E 58, 6027. But before going into the details of the instability, lets discuss generally some mechanisms of mass transport.

1.1 Mass transport and chemical potential

We introduce a new (non-elastic, non-equilibrium) piece of physics: mass transport along the surface of the solid. The surface evolves with a normal velocity v_n, which is driven by variation of the chemical potential density μ (the chemical potential is the relevant thermodynamic quantity because we are talking about mass transport). Mathematically speaking we say that

$$v_n = \boldsymbol{\mathcal{D}}(\mu) \ , \tag{1}$$

where $\boldsymbol{\mathcal{D}}(\cdot)$ is a differential operator that depends on the physical nature of the mass transport.

We may think of several mass transport processes. When the solid is in equilibrium with its liquid phase (or gaseous phase), mass transport can take place by melting-recrystallization (or evaporation-condensation). In both cases, the transport law takes the form

$$v_n \sim -\Delta\mu \ , \tag{2}$$

where $\Delta\mu = \mu_s - \mu_l$ is the chemical potential difference between the solid and liquid phase (or gaseous phase μ_g).

Another possible process would be surface diffusion, which is the surface analog of ordinary bulk diffusion. In this case, surface gradients of μ drive a material flux J_s

$$J_s \sim -\frac{\partial\mu}{\partial s} \ , \tag{3}$$

where s is the arclength parameterization of the surface. Mass conservation implies

$$v_n \sim -\frac{\partial J_s}{\partial s} \sim \frac{\partial^2\mu}{\partial s^2} \ . \tag{4}$$

Putting the prefactors in, we end up with

$$v_n = \frac{D}{\gamma}\frac{\partial^2\mu}{\partial s^2} \ , \tag{5}$$

where D, whose dimension is length^4/time, is proportional to the surface diffusion coefficient and γ is the surface tension. We stress that the evolution of the surface, encapsulated in v_n is a non-equilibrium dissipative process.

The next step would be to write down an expression for the chemical potential density (in the presence of a liquid phase, we are of course interested in the chemical potential difference between the solid and the liquid). Let us first write down the answer and then try to understand its origin. The chemical potential density contains two contributions, one is an elastic strain energy contribution near the surface and the other is a surface contribution

$$\mu = \mu_e + \mu_s = \frac{1-\nu^2}{2E}\left(\sigma_{tt} - \sigma_{nn}\right)^2 + \gamma\kappa \ , \tag{6}$$

where μ_e and μ_s are the elastic and surface energy contributions to the chemical potential density. t and n are the tangent and normal to the surface, respectively, γ is the surface tension/energy as above and κ is the surface curvature.

If the surface is not in contact with its liquid phase, i.e. $\sigma_{nn} = 0$ (note that $\sigma_{nt} = 0$ with or without a liquid), the elastic contribution is simply the elastic strain energy in the solid. If the surface is in equilibrium with its liquid phase, then there is a finite pressure of magnitude $|\sigma_{nn}|$ also in the liquid, and the chemical potential difference depends on the difference $\sigma_{tt} - \sigma_{nn}$. This result also shows that under hydrostatic conditions in the solid, $\sigma_{tt} = \sigma_{nn}$ there's no elastic contribution (and the effect we are interested in will disappear).

What about the surface energy contribution? The change in the Gibbs free energy due to surface area changes is $dG = \gamma dA$. Since the (surface) chemical potential is the change of G with the number of particles of total volume dV added to the surface, $\mu = dG/dV$, we should ask ourselves how the surface area changes when we add a volume dV of material to a surface (we stress that dV is not an incremental deformation, but rather represents a piece of a material). That obviously depends on the curvature of the surface.

For a convex/concave surface an addition of a particle of volume dV results in an increase/decrease in the surface area by an amount $dA \sim dV\kappa$, where κ is the signed curvature (assumed positive for convex surfaces). To make this absolutely clear, consider a spherical surface of radius R and the addition of an infinitesimal mass element of volume dV. The change in the sphere's volume is given by $4\pi R^2 dR = dV$, and hence the change in the effective radius is $dR = dV/4\pi R^2$. Hence, the change is the area is $dA = d(4\pi R^2) = 8\pi R dR = 2dV/R \sim dV\kappa$. For a spherical cavity, we get the same result with a minus sign. Therefore, the surface energy contribution to the chemical potential density is $\gamma\kappa$.

Finally, we assume that the growth velocity of these protrusions v_n is fast, and is proportional to the difference in chemical potential between the solid μ_s and liquid μ_l phases, i.e.

$$v_n = -k_\nu \mu = -k_\nu \left[\frac{1-\nu^2}{2E}\left(\sigma_{tt} - \sigma_{nn}\right)^2 + \gamma\kappa\right] \ . \tag{7}$$

We also assume that v_n is fast, but nothing compared to the speeds of sound in the material, i.e. $v_n \ll c_s, c_d$ (as we want to consider the quasi-static case).

Realistically the material may have surface fluctuations, and is not perfectly flat. What happens to such a small fluctuation in the interface? What happens if the material is subjected to constant uniaxial strain? Our goal is to derive analytically an expression for $\sigma_{tt} - \sigma_{nn}$ which, as you can see from Eq. (6), has dramatic effect on μ.

1.2 Background and intuition

Consider a solid, say of rectangular shape, under the application of uniaxial tension (or compression) of magnitude σ_0 (the non-hydrostatic conditions are important). The stress is small and the response is linear elastic. The solution is simply that of homogeneous stress and it is stable (i.e. , if a compressive stress is applied, we assume the conditions for buckling are not met).

Now imagine this solid is in contact with its melt. Plugging the expression for μ in Eq. (6) into Eq. (7) we obtain a dynamic equation that can be used to study the stability of the surface against small perturbations. To be absolutely clear about the last point, we denote the deviation of the surface from being flat by $h(x,t)$, where x is the load application direction. Both v_n and μ can be expressed in terms $h(x,t)$. For a flat surface, $h(x,t) = 0$, $\kappa = 0$ and μ is constant $\mu = \frac{1-\nu^2}{2E}\sigma_0^2$ (here $\sigma_0 = \sigma_{tt} - \sigma_{nn}$). This, of course, implies $v_n = 0$, as expected.

To understand what happens when the surface is not flat, we should introduce a small spatiotemporal perturbation $h(x,t) \neq 0$ and see if it grows or decays in time. Before we do that, let us first try to make a rough estimate. For that aim, consider a square wave perturbation of the surface, with an amplitude a and a wavelength λ. Let us estimate the change in the Gibbs free energy due to the perturbation. On the one hand, the protruding parts of the perturbation are far less stressed than they were when the surface was flat. Therefore, the elastic energy (per wavelength) is reduced roughly by

$$\Delta G_e \sim -\frac{\sigma_0^2}{2E}\frac{\lambda a}{2} \ . \tag{8}$$

The surface energy is increased due to the creation of new surface of size $2a$ (again per wavelength) by

$$\Delta G_s = 2\gamma a \ . \tag{9}$$

Therefore, the total variation of the Gibbs free energy is given by

$$\Delta G = \Delta G_e + \Delta G_s \sim -\frac{\sigma_0^2}{2E}\frac{\lambda a}{2} + 2\gamma a \ . \tag{10}$$

The important insight here is that there is a competition between an elastic effect, that tends to reduce the free energy (a destabilizing effect), and a surface effect that tends to increase it (a stabilizing effect). For sufficiently small wavelengths, the surface term penalizes more, and stability is expected. For sufficiently large wavelengths, the elastic term wins and the free energy is reduced. The critical wavelength scales as

$$\lambda_c \sim \frac{\gamma E}{\sigma_0^2} \ , \tag{11}$$

where wavelengths satisfying $0 < \lambda < \lambda_c$ are stable and $\lambda > \lambda_c$ are unstable. While this is a crude estimate, it gives us some insight into the physics behind the instability and essentially the right answer (as we will see soon). Actually it is no more than a dimensional analysis, which is in general quite a powerful tool.

1.3 Elastic equations

Lets take a more systematic approach and see properly how a linear stability analysis is done.

Consider an isotropic elastic material, under plane-strain conditions (reducing the problem to 2D) — we set $\epsilon_{zz}=0$. Hooke's law implies

$$\sigma_{ij}=\frac{E}{1+\nu}\left(\epsilon_{ij}+\frac{\nu}{1-2\nu}\epsilon_{kk}\delta_{ij}\right) \ , \tag{12}$$

with E being the Young's modulus and ν being the Poisson's ratio.

Now consider such a material to be rectangular, of length L in the x direction and filling the $y\leq 0$, with a free surface at $y=0$ as shown in Fig. 1. The remaining space is filled with a liquid. We first constrain the material to $\epsilon_{xx}=0$. *Under these conditions*, we have at the top free boundary

$$\boldsymbol{\sigma}\left(x,y=0\right)\cdot\hat{\boldsymbol{n}}=\left(\sigma_{xy},\sigma_{yy}\right)^T=\left(0,-p_l\right)^T \ , \tag{13}$$

where p_l is the pressure applied by the melt.

As we have a linear elastic problem in 2D, we can use all the machinery from linear elasticity. Lets try and solve the elastic problem using the Airy stress function $\chi\left(x,y\right)$, defined as

$$\begin{aligned}\sigma_{xx} &= \partial_{yy}\chi \ , &(14)\\ \sigma_{yy} &= \partial_{xx}\chi \ , &(15)\\ \sigma_{xy} &= -\partial_{xy}\chi \ . &(16)\end{aligned}$$

We also know that the Airy stress function should satisfy the bi-Laplacian equation $\nabla^2\nabla^2\chi=0$.

What are the boundaries, and what are the corresponding boundary conditions? We have a free boundary at $y=0$, and for $x=\pm\frac{L}{2}$, for which we have

$$\begin{aligned}\sigma_{nn} &= -p_l \ , &(17)\\ \sigma_{tn} &= 0 \ , &(18)\end{aligned}$$

here $\sigma_{tn}=\hat{\boldsymbol{t}}\cdot\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}$. If we impose stresses in the $\hat{\boldsymbol{x}}$ direction we have an additional stress σ_0 in σ_{xx}, so we have to add this in the $\hat{\boldsymbol{x}}$ direction. Note that unlike in Eq. (13), here the boundaries are not necessarily flat. Because of this, we cannot a priori say that $\hat{\boldsymbol{t}}=\hat{\boldsymbol{x}}$, or that $\hat{\boldsymbol{n}}=\hat{\boldsymbol{y}}$ — these geometric vectors are going to change in space. Explicitly, the boundary conditions are

$$\begin{aligned}p_l+n_x^2\sigma_{xx}+2n_xn_y\sigma_{xy}+n_y^2\sigma_{yy} &= 0 \ , &(19)\\ n_xt_x\sigma_{xx}+n_xt_y\sigma_{xy}+n_yt_x\sigma_{yx}+n_yt_y\sigma_{yy} &= 0 \ . &(20)\end{aligned}$$

Eventually we will be interested in surface perturbation to the top face of the material. We will describe the top free surface of the material as $h\left(x,t\right)$ (sometimes referred to as the Monge's gauge), from which we derive the normal and tangent vectors as

$$(n_x, n_y) = \frac{1}{\sqrt{1+(\partial_x h)^2}}(-\partial_x h, 1) \ , \tag{21}$$

$$(t_x, t_y) = \frac{1}{\sqrt{1+(\partial_x h)^2}}(1, \partial_x h) \ . \tag{22}$$

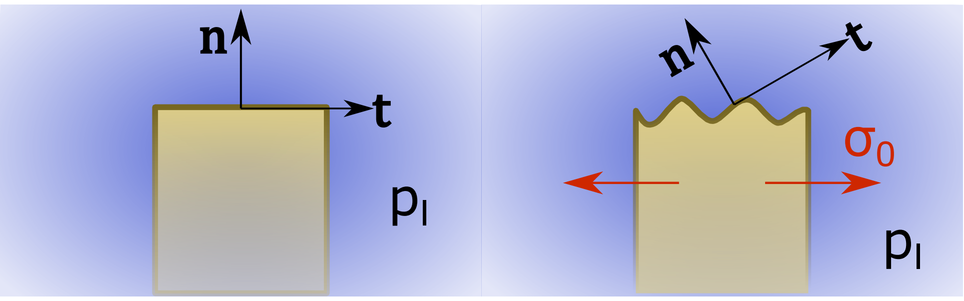

Figure 1: Left: a material in a melt, in the presence of an isotropic pressure p_l. Right: the same material subjected to uniaxial stress σ_0 in the x direction, and a spatial perturbation of the upper surface.

1.4 Perturbative expansion

Solving the elastic problem for any given surface is going to be challenging, and may be tackled numerically. Instead we are going to consider perturbations to the flat surface we started with, and expand the problem (and the solution) in orders of a small parameter δ. We anticipate that the stress tensor $\boldsymbol{\sigma}$ will contain contributions that are spatially independent, $\boldsymbol{\sigma}^{(0)}$, contributions that are first order in the small parameter δ, $\boldsymbol{\sigma}^{(1)}$, etc. Generically, we write $\boldsymbol{\sigma} = \boldsymbol{\sigma}^{(0)} + \delta \cdot \boldsymbol{\sigma}^{(1)} + \delta^2 \cdot \boldsymbol{\sigma}^{(2)} + ...$ Similarly, we can expand

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{(0)} + \delta \cdot \boldsymbol{\sigma}^{(1)} + \delta^2 \cdot \boldsymbol{\sigma}^{(2)} + \dots \ , \tag{23}$$

$$\chi = \chi^{(0)} + \delta \cdot \chi^{(1)} + \delta^2 \cdot \chi^{(2)} + \dots \ , \tag{24}$$

$$h = h^{(0)} + \delta \cdot h^{(1)} + \delta^2 \cdot h^{(2)} + \dots \ . \tag{25}$$

Let us first deal with the zeroth order, and consider contributions in the absence of spatial perturbation. For the zeroth order $\boldsymbol{n}^{(0)} = (0, 1)$, and $\boldsymbol{t}^{(0)} = (1, 0)$. Eq. (19) yield

$$n_y^2 \sigma_{yy}^{(0)} = -p_l \ , \tag{26}$$

and the second condition vanishes identically (we have no shear stresses to first order $\sigma_{xy}^{(0)} = 0$). From the definition of the Airy stress function Eq. (14) its clear that χ must depend on x and y in order to produce these conditions. We then have

$$\chi^{(0)}(x, y) = -p_l \frac{x^2}{2} + (\sigma_0 - p_l)\frac{y^2}{2} \ , \tag{27}$$

where we satisfy that $\sigma_{xx} = \sigma_0 - p_l$ originating from both the hydrostatic pressure applied by the surrounding liquid p_l and the applied stress σ_0.

Is this flat solution stable against spatial perturbations? Consider a spatial perturbation of the form $h^{(1)}(x,t) = h_0 e^{iq_x x - \omega t}$, and the consequent perturbation $\chi^{(1)}$ in Fourier space. The only spatial wavelength available is q_x, and we will be considering only linear terms, so $\chi^{(1)}$ must also have some periodicity in the x direction with the same q_x.

Lets see what the bi-Laplace equation has to tell us about the relation between wavelengths in the x and y directions. First, plug in to the bi-Laplace equation $\chi = e^{iq_x x + iq_y y}$, giving $\left(q_x^2 + q_y^2\right)^2 = 0$, implying that for a real q_x, we must have $q_y = \pm i q_x$. As we are considering the domain $y \leq 0$, it makes sense that $\chi^{(1)}$ will exponentially-decay in the bulk in the y direction. Finally, $\chi^{(1)}$ could also depend on time. We can thus write $\chi^{(1)} = (A + By) e^{iq_x x + q_x y + \omega t}$ — higher multiples of y will not obey the bi-Laplace equation.

Plugging in to our definition of Eq. (14), we express the stresses $\boldsymbol{\sigma}$ as

$$\begin{aligned}
\sigma_{xx} &= (\sigma_0 - p_l) + \delta q_x \left[2B + q_x (A + By)\right] e^{iq_x x + q_x y + \omega t} \ , && (28)\\
\sigma_{yy} &= -p_l - \delta q_x^2 (A + By) e^{iq_x x + q_x y + \omega t} \ , && (29)\\
\sigma_{xy} &= i q_x \delta \left[B + q_x (A + By)\right] e^{iq_x x + q_x y + \omega t} \ . && (30)
\end{aligned}$$

We would like to use the boundary conditions of Eq. (19), but we first need to expand both $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{t}}$ to first order in δ. We have now for the top boundary

$$\begin{aligned}
(n_x, n_y) &\simeq \left(-i q_x \delta h^{(1)}, 1\right) \ , && (31)\\
(t_x, t_y) &\simeq \left(1, i q_x \delta h^{(1)}\right) \ . && (32)
\end{aligned}$$

We now use our previous expressions for the boundary conditions Eq. (19) to first order

$$\begin{aligned}
\sigma_{yy}^{(0)} + \delta \sigma_{yy}^{(1)} + \mathcal{O}\left(\delta^2\right) &= -p_l \ , && (33)\\
\delta \left[-i q_x \sigma_0 h(x,t) + \sigma_{xy}^{(1)}\right] + \mathcal{O}\left(\delta^2\right) &= 0 \ . && (34)
\end{aligned}$$

Upon substitution of Eq. (28), and evaluating the expressions at the free surface, $y = 0$, we have

$$\begin{aligned}
A &= 0 \ , && (35)\\
B &= -h_0 \sigma_0 \ . && (36)
\end{aligned}$$

Substituting into σ_{tt} and σ_{nn} we have that

$$\sigma_{tt} - \sigma_{nn} = \sigma_0 \left[1 - 2\delta |q_x| h^{(1)}(x,t)\right] \ . \tag{37}$$

Using this expression in Eq. (6) and collecting contributions up to linear order in the small parameter δ, we have

$$\mu = \frac{1 - \nu^2}{2E} \sigma_0^2 \left(1 - 4\delta q_x h^{(1)}(x,t)\right) + \gamma \delta q_x^2 h^{(1)}(x,t) \ . \tag{38}$$

The zeroth order contribution is positive, meaning that a stress increases the solid chemical potential, and renders it unfavorable (which causes the solid to melt). We shall ignore this contribution for now (in the original paper it was balanced by a gravitational force).

The linear order contribution is more interesting. Relating $v_n \simeq \frac{\partial h}{\partial t}$, and plugging in our result from Eq. (7) yields

$$\omega = k_v \left[\frac{2\sigma_0^2 \left(1-\nu^2\right)}{E} q_x - \gamma q_x^2 \right] \ , \tag{39}$$

implying that non-zero σ_0 destabilize the surface perturbation while the surface tension stabilizes it. Any perturbation with wavenumber smaller than $q_x^c = \frac{2(1-\nu^2)}{E\gamma}\sigma_0^2$ will grow according to this.