Non-Equilibrium Continuum Physics **TA session #9**

09/06/2021

Perturbative expansion and Visco-Elasticity

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

We first revisit the Asaro–Tiller–Grinfeld (ATG) instability discussed in class, 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.

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

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

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. 2. 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

$$\boldsymbol{\sigma}\left(x, y=0\right) \cdot \hat{\boldsymbol{n}} = \left(\sigma_{xy}, \sigma_{yy}\right)^T = \left(0, -p_l\right)^T \ , \tag{2}$$

where p_l is the pressure applied by the melt.

We now introduce an additional piece of physics — the material may grow in the normal direction by deposits that stick to the surface for example. 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.

$$v_n = -k_\nu\left(\mu_s - \mu_l\right) \equiv -k_\nu \Delta\mu \ . \tag{3}$$

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?

In class you have seen that

$$\Delta\mu = \frac{1-\nu}{2E}\left(\sigma_{tt} - \sigma_{nn}\right)^2 + \gamma\kappa \tag{4}$$

where $\sigma_{tt} = \hat{\boldsymbol{t}} \cdot \boldsymbol{\sigma} \cdot \hat{\boldsymbol{t}}$ and $\sigma_{nn} = \hat{\boldsymbol{n}} \cdot \boldsymbol{\sigma} \cdot \hat{\boldsymbol{n}}$ are the tangential and normal components of $\boldsymbol{\sigma}$, γ is the surface tension and κ is the interface curvature. In class you have guessed the expression $\sigma_{tt}-\sigma_{nn}$ — our goal is to derive analytically an expression for $\sigma_{tt}-\sigma_{nn}$ which, as you can see from Eq. (4), has dramatic effect on $\Delta\mu$.

Back to our linear elastic material. 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 $\chi(x,y)$, defined as

$$\begin{aligned}\sigma_{xx} &= \partial_{yy}\chi \ , &(5)\\ \sigma_{yy} &= \partial_{xx}\chi \ , &(6)\\ \sigma_{xy} &= -\partial_{xy}\chi \ . &(7)\end{aligned}$$

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

$$\begin{aligned}\sigma_{nn} &= -p_l \ , &(8)\\ \sigma_{tn} &= 0 \ , &(9)\end{aligned}$$

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. (2), 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

$$\begin{aligned}p_l + n_x^2\sigma_{xx} + 2n_xn_y\sigma_{xy} + n_y^2\sigma_{yy} &= 0 \ , &(10)\\ n_xt_x\sigma_{xx} + n_xt_y\sigma_{xy} + n_yt_x\sigma_{yx} + n_yt_y\sigma_{yy} &= 0 \ . &(11)\end{aligned}$$

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 $h(x,t)$ (sometimes referred to as the Monge's gauge), from which we derive the normal and tangent vectors as

$$\begin{aligned}(n_x,n_y) &= \frac{1}{\sqrt{1+(\partial_x h)^2}}\left(-\partial_x h, 1\right) \ , &(12)\\ (t_x,t_y) &= \frac{1}{\sqrt{1+(\partial_x h)^2}}\left(1, \partial_x h\right) \ . &(13)\end{aligned}$$

1.1 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 $\boldsymbol{\sigma}=\boldsymbol{\sigma}^{(0)}+\delta\cdot\boldsymbol{\sigma}^{(1)}+\delta^2\cdot\boldsymbol{\sigma}^{(2)}+\ldots$. Similarly, we can expand

$$\begin{aligned}\boldsymbol{\sigma} &= \boldsymbol{\sigma}^{(0)}+\delta\cdot\boldsymbol{\sigma}^{(1)}+\delta^2\cdot\boldsymbol{\sigma}^{(2)}+\ldots \ , &(14)\\ \chi &= \chi^{(0)}+\delta\cdot\chi^{(1)}+\delta^2\cdot\chi^{(2)}+\ldots \ , &(15)\\ h &= h^{(0)}+\delta\cdot h^{(1)}+\delta^2\cdot h^{(2)}+\ldots \ . &(16)\end{aligned}$$

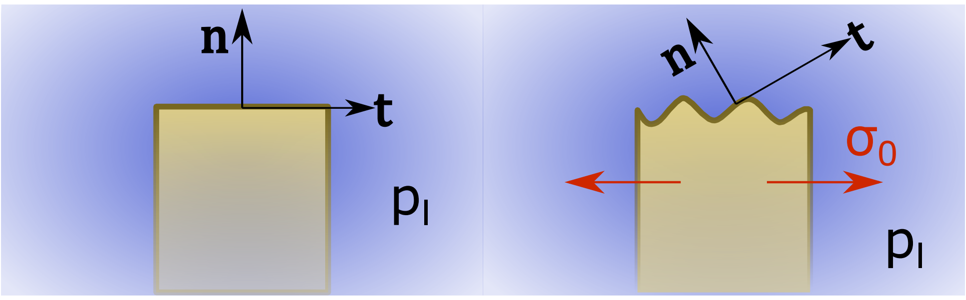

Figure 1: Left: a material in a melt, in the presence of an isotropic pressure p_l. Right: the same material subjected to uniaxial stress σ_0 in the x direction, and a spatial perturbation of the upper surface.

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. (10) yield

$$n_y^2 \sigma_{yy}^{(0)} = -p_l \ , \tag{17}$$

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. (5) its clear that χ must depend on x and y in order to produce these conditions. We then have

$$\chi^{(0)}(x,y) = -p_l \frac{x^2}{2} + (\sigma_0 - p_l)\frac{y^2}{2} \ , \tag{18}$$

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. (5), we express the stresses $\boldsymbol{\sigma}$ as

$$\begin{aligned} \sigma_{xx} &= (\sigma_0 - p_l) + \delta q_x \left[2B + q_x (A + By)\right] e^{iq_x x + q_x y + \omega t} \ , & (19)\\ \sigma_{yy} &= -p_l - \delta q_x^2 (A + By)\, e^{iq_x x + q_x y + \omega t} \ , & (20)\\ \sigma_{xy} &= iq_x \delta \left[B + q_x (A + By)\right] e^{iq_x x + q_x y + \omega t} \ . & (21) \end{aligned}$$

We would like to use the boundary conditions of Eq. (10), 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

$$\begin{aligned} (n_x, n_y) &\simeq \left(-iq_x \delta h^{(1)}, 1\right) \ , & (22)\\ (t_x, t_y) &\simeq \left(1, iq_x \delta h^{(1)}\right) \ . & (23) \end{aligned}$$

We now use our previous expressions for the boundary conditions Eq. (10) to first order

$$\begin{aligned} \sigma_{yy}^{(0)}+\delta\sigma_{yy}^{(1)}+\mathcal{O}\left(\delta^{2}\right) &= -p_{l}\ , \qquad (24)\\ \delta\left[-iq_{x}\sigma_{0}h\left(x,t\right)+\sigma_{xy}^{(1)}\right]+\mathcal{O}\left(\delta^{2}\right) &= 0\ . \qquad (25)\end{aligned}$$

Upon substitution of Eq. (19), and evaluating the expressions at the free surface, $y=0$, we have

$$\begin{aligned} A &= 0\ , \qquad (26)\\ B &= -h_{0}\sigma_{0}\ . \qquad (27)\end{aligned}$$

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

$$\sigma_{tt}-\sigma_{nn}=\sigma_{0}\left[1-2\delta|q_{x}|h^{(1)}\left(x,y,t\right)\right]\ , \qquad (28)$$

which is Eq.(8.18) in Eran's lecture notes (replacing q_x with k).

In the lectures you have seen how this yields an instability — relating $v_n \simeq \frac{\partial h}{\partial t}$, and plugging in our result from Eq. (28) with Eq. (4) and Eq. (3) yields

$$\omega=k_{v}\left[\frac{2\sigma_{0}^{2}\left(1-\nu^{2}\right)}{E}q_{x}-\gamma q_{x}^{2}\right]\ , \qquad (29)$$

implying that non-zero σ_0 destabilize the surface perturbation while the surface tension stabilizes it.

2 Visco-elasticity

As Eran mentioned in class, in reality many solids exhibit behaviors that deviate somewhat from the linear elastic theory we developed so far. An idealized elastic solid under small stress will respond instantaneously to the strain level determined by the elastic moduli. Realistically, solids continue to accumulate strains on longer time-scales, a behavior called "creep". Imposing a small strain on an idealized elastic solid will again result in an instantaneous stress jump. Realistically, solids exhibit long time-scale stress relaxation. We would like to understand these behaviors in the framework of visco-elasticity.

First, lets consider solids on the microscopic level — imagine a crystalline solid composed of harmonically-interacting particles. Under small deformation particles would displace, increasing the overall energy of the system — its these deviations that we have considered in our course-graining TA#3 that gave rise to the elastic constants. However, the local neighborhood of each of the particles is not changed at all — they still interact with their previous neighbors. Both thermal energy in the environment and the elastic energy are not enough to displace particles as the interactions "hold" the particles in their place.

What happens when we consider a liquid phase? Imagine a liquid phase of short-range interacting particles confined to a certain volume. You know from your high-school and undergrad studies that the particles will rearrange because of the thermal energy distribution. Moreover, if we impose forces on the box, the particles will displace as well, always changing their neighbors. There are two options: (i) either the particles will somehow counter the imposed force, arriving at a new equilibrium (this is the case under compression), or (ii) they will keep on flowing (this happens under shear forces).

These configurational changes in the liquid phase are almost the definition of a liquid. You can get the feeling that while the supplemented energy in the solid case was insufficient to make particles move around, in the liquid case its exactly what they do. These rearrangements give rise to Brownian motion (fluctuations) and to viscous damping (dissipation) under applied force.

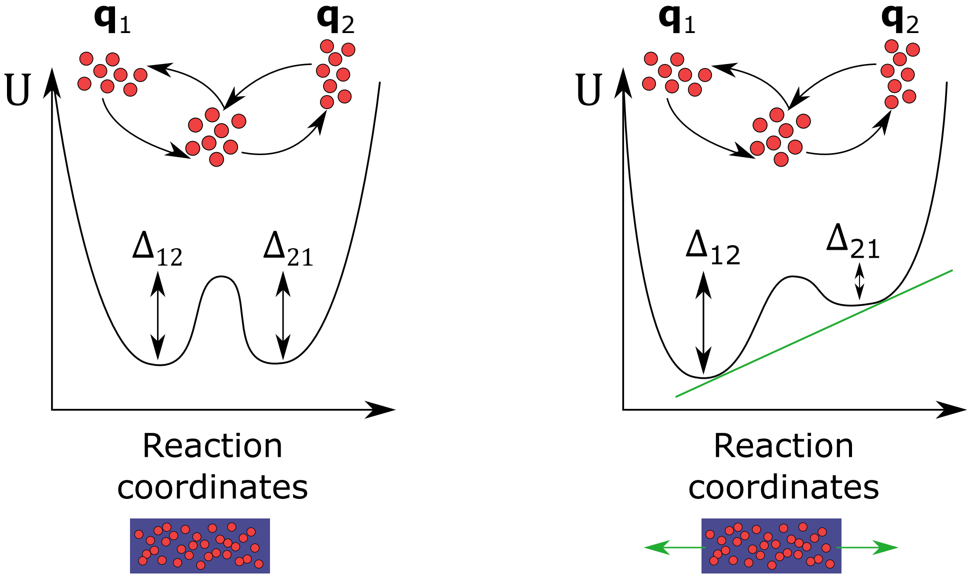

Figure 2: Left: at rest the barrier between the two configurations is symmetric. Right: once stress is applied, the barrier is no longer symmetric, favoring one state over another.

Lets consider things more concretely, and focus on a small number of particles placed in a thermal bath of temperature T. There is an entire phase space for the available configurations of these particles, but we shall consider things schematically, in the "reaction coordinates". We can probe the energy landscape of these particles, and obtain the energy $U(\boldsymbol{q})$ for each configuration $\boldsymbol{q}$ in the phase space. Its very probable, that some configurations will admit lower energy U (say, when all particles are placed at the "rest-lengths" of the interactions) , while others will have higher energies U (for example when all the bonds are stretched). We can plot these energy states as a function of the reaction coordinates.

Usually, to pass from one energetic minimum to another, there is an energetic barrier the system has to cross. Imaging these particles going from one configuration $\boldsymbol{q}_1$ with energy U_1 to another one $\boldsymbol{q}_2$ of energy U_2 — some of the particles will have to move in the process, and in order to make them move we must invest energy in to the system. We will denote the energy we have to invest to cross from $\boldsymbol{q}_1$ to $\boldsymbol{q}_2$ as Δ_{12}. Similarly, if we were to start from configuration $\boldsymbol{q}_2$ crossing back to $\boldsymbol{q}_1$, we would have to invest Δ_{21}.

Now, consider the thermal fluctuations available to these particles in equilibrium. You know from statistical mechanics that this is the canonical ensemble, and the proper way to weight states is using the Boltzmann factor e^{-U_1/k_BT} and e^{-U_2/k_BT} for the states $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ respectively. Crossing between the two states is proportional to the energy barrier between the two states, $P\left(\Delta_{12}\right)\sim e^{-\Delta_{12}/k_BT}$ — same goes to the inverse process. The rate of going from $\boldsymbol{q}_1$ to $\boldsymbol{q}_2$ is proportional to the probability of fluctuation, divided by some microscopic time-scale τ_0. This result is associated with Arrhenius (1889), Eyring (1935) and Kramers (1940), see the Supplementary Materials under the course page.

Now lets consider dimensional analysis in light of what we have observed above — we have seen that liquid particles diffuse, i.e. there is a diffusion constant involved. We know that the relevant time-scale for particle rearrangements is inverse of the rate, i.e. $\tau\sim\tau_0 e^{\Delta/k_BT}$. Finally, we know that our bunch of particles accommodate a typical volume in our system, so there is a length-scale a associated with this volume $a^3=V$. Using the dimensions of the last two quantities, we have that

$$D\sim\frac{a^2}{\tau}\ . \tag{30}$$

Consider now a specific configuration of the small particle collection and associate $\boldsymbol{q}_1$ with alignment in the x direction, and $\boldsymbol{q}_2$ to the same structure aligned in the y direction. As there is nothing in space that prefers one direction or another, the total energy will be the same, i.e. $U_1=U_2$, and $\Delta_{12}=\Delta_{21}$ — the particles must still overcome a barrier in order to rearrange from $\boldsymbol{q}_1$ to $\boldsymbol{q}_2$, but the initial and final energy states are the same.

Next, consider what happens if we impose stress (say, elongation) in the x direction. Obviously, the configuration that is aligned in the x direction will be more favorable as the entire material feels forces in that direction. Now, $U_1<U_2$, and the crossing barriers $\Delta_{12}>\Delta_{21}$, as a consequence.

Lets now ask, what energy scale emerged from our loading, and how can we accommodate it into Δ_{12} and Δ_{21}? If we impose a stress σ, we need a typical volume to make $\sigma\Omega$ an energy scale. You may recall that we have already introduced a molecular length a, and indeed we may suppose that now $\Delta_{12}=\Delta_0+\sigma\Omega$, and $\Delta_{21}=\Delta_0-\sigma\Omega$. The emerging rate of rearrangements along the loading direction will be simply the forward transformations (to the x alignment), minus the inverse rearrangements

$$\dot{\epsilon}\sim\frac{1}{\tau_0}\left[\exp\left(-\frac{\Delta_0-\sigma\Omega}{k_BT}\right)-\exp\left(-\frac{\Delta_0+\sigma\Omega}{k_BT}\right)\right]\sim\frac{1}{\tau}\sinh\left(\frac{\sigma\Omega}{k_BT}\right)\ . \tag{31}$$

If we reverse our external loading, i.e. take $\sigma\to-\sigma$, we have that $\dot{\epsilon}\left(-\sigma\right)=-\dot{\epsilon}\left(\sigma\right)$, which is exactly what we want — we now impose the inverse bias.

In the linear response theory we defined the elastic constants as the proportionality factor relating the stress $\boldsymbol{\sigma}$ and the strain $\boldsymbol{\epsilon}$ under small deformations, i.e. we have used $\boldsymbol{C}=\lim\limits_{\epsilon\to0}\frac{\boldsymbol{\sigma}}{\boldsymbol{\epsilon}}$, which is very much like taking a derivative. We now use a similar relation, and define the Newtonian viscosity as $\eta=\lim\limits_{\dot{\epsilon}\to0}\frac{\sigma}{\dot{\epsilon}}$. Just to check, consider an elastic solid under applied strain — the strain rate is $\dot{\epsilon}=0$, and we get $\eta\to\infty$ for an elastic solid.

By plugging in to this definition Eq. (31), we get that

$$\eta\sim\frac{k_BT}{\Omega}\tau_0\exp\left(\frac{\Delta}{k_BT}\right)\ . \tag{32}$$

You can now see explicitly that the viscosity is affected by the temperature, but also by the energy barriers in the system.

Another cool aspect here is the Stoke's-Einstein relations between the viscosity η and the diffusion coefficient D. You can see that $D \cdot \eta \sim \frac{k_B T}{a}$, which is one form of these relations.

So this all discussion was for liquids. How are solids related here anyhow? Solids may have spots that are prone to rearrangements — for example, think of areas in which particles are more spaced, giving more available volume for rearrangements, or particles that interact with less neighbors. η will surely be affected by the abundance of these "soft" areas in the material, so in fact there is a missing pre-factor in Eq. (32) to accommodate for the abundance of these spots.

How do these microscopic considerations relate to the continuum level? Well, for one thing we have already defined a "continuum" quantity, that is $\eta = \lim\limits_{\dot{\epsilon}\to 0} \frac{\sigma}{\dot{\epsilon}}$. Lets see if this is consistent with thermodynamics.

Back in the day, Eran showed you that the second law of thermodynamics splits into two inequalities. One of them was

$$\boldsymbol{\sigma} : \boldsymbol{D} - \rho \dot{u} + T \rho \dot{s} \geq 0 \ , \tag{33}$$

where $\boldsymbol{\sigma}$ is the standard stress tensor, $\boldsymbol{D}$ was the deformation rate(!), ρ is the density, u is the internal energy density, T is the temperature, and s is the entropy density. Consider a material that does not contain an elastic energy contribution — the internal energy density u depends only on the entropy s. We now use the chain rule $\dot{u} = \frac{\partial u}{\partial s} \dot{s}$, but $\frac{\partial u}{\partial s} \equiv T$. So, we have cancelation, leading to $\boldsymbol{\sigma} : \boldsymbol{D} \geq 0$. We now denote $\boldsymbol{D}$ by $\dot{\boldsymbol{\epsilon}}$, as the two are equivalent to lowest order.

Now behold! We have defined $\eta = \lim\limits_{\dot{\boldsymbol{\epsilon}}\to 0} \frac{\boldsymbol{\sigma}}{\dot{\boldsymbol{\epsilon}}}$, and upon rearranging we have $\boldsymbol{\sigma} \sim \eta \dot{\boldsymbol{\epsilon}}$. Plugging this into the inequality above yields a quadratic function $\eta \dot{\boldsymbol{\epsilon}} : \dot{\boldsymbol{\epsilon}}$ which is positive by definition! So in fact, our results obey the second law of thermodynamics.