Lecture 1 The Cavity

Purpose of the Course

Scientists have acquired many powerful tools over centuries. A tool was invented by Newton for one job. Laplace sharpened it. A third person, Einstein, later discovered that he had a new job done by combining the tool with another tool invented by Maxwell. The tools become popular and are efficiently delivered in universities. To save time and transmit more tools between generations, teachers like me have come up with this dubious idea: a lean and mean curriculum with no redundancy. However, there is a danger that students are given tools without an instruction to use them. Loaded in many courses are formalities and abstractions, chosen to save time by some, and to hide ignorance by others. Teachers have little time to show the excitement of using the tools to make a new discovery.

In this course, I'll use examples to show how complex phenomena are understood by integrating ideas that you've already learnt. Once you have uncovered a few things for yourself, maybe learning new ideas becomes a lot easier. Now you have a purpose in mind, a problem dear to your own heart, when you learn. I don’t really have a curriculum, or a definite set of material that I must cover. I hope to *uncover* a few things for you. We’ll make up a curriculum toward the end of the semester, so that the university will be happy about the course, and you feel that you have spent time wisely. For now, I’ll send you an outline of the course I taught in 2003 at Princeton. I know some topics better than others. If you know a topic better than I do, please speak up.

You’ll have to work. Feel free to discuss weekly assignments with anyone, but hand in your write up individually. The weekly assignments will contribute 60% of the grade. To reward people who really understand the weekly assignments, the final exam will draw heavily on the weekly assignments. The final exam will be close-book, and contribute 40% of the grade.

To bring life to the course, I'll choose topics dear to me at the moment. They may or may not be popular topics in mechanics of the day, and may have loose ends and uncertainties. But that doesn't matter so long as we enjoy them. If you find that you are distressed with the uncertainties, try to cope with it like a good scientist. Relax. Have fun.

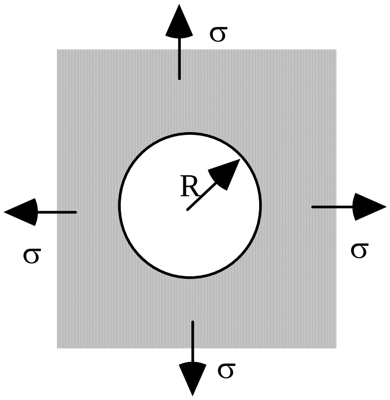
Representative Phenomena to be Discussed

- Cavitation
- Electromigration
- Self-assembled quantum dots
- Programmable assembly of molecules on solid surfaces
- Ratcheting plastic deformation

A Cavity in a Solid

A solid contains a spherical cavity, radius R, subject to a hydrostatic stress σ. For now, we assume that the solid is stiff so we ignore its deformation. The cavity can still change its size by a special mechanism: atoms diffuse through the solid between the cavity surface and the external surface. We will concentrate in this lecture on the question, *Will the cavity shrink or enlarge?* We will consider the diffusion process in some detail in the next lecture, and answer the question, *How fast will the cavity change its size?*

Two forces act on the solid: the surface tension, and the external stress. First consider the action of the surface tension. At a finite temperature, atoms move in the solid. Most time, an atom just vibrates around its lattice site. The vibration amplitude is smaller than the lattice spacing, and the cavity neither enlarges nor shrinks. Occasionally, an atom near the cavity surface jumps out of its lattice site, and falls on the cavity surface. This has two consequences: a lattice site is vacant, and the cavity becomes one-atom smaller. The vacant site in the solid will soon be filled by another atom. If the vacant site is filled by the atom that just jumped onto the surface, everything goes back to its original state. If the vacant site is filled by one of other adjacent atoms, the vacancy *diffuses* further into the solid, eventually disappears at the external surface. The cavity becomes smaller, and therefore has a smaller surface energy. Recall that thermodynamics requires a process to reduce the free energy of the system. *If the surface energy acts alone, the free energy decreases when the cavity shrinks.*



Next consider the action of the stress on the external surface. When an atom in the solid, near the external surface, jumps out of its lattice site and falls on the surface, the stress does work, and thereby reduces the potential energy. (Imagine that the stress is applied by a weight to see that the potential energy indeed decreases.) The vacant lattice site will diffuse further into the solid, and eventually disappear at the cavity surface. *If the tensile stress acts alone, the free energy decreases when the cavity enlarges.*

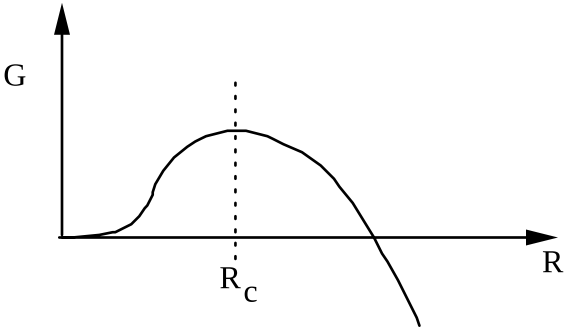
In summary, the surface tension strives to pull atoms from the external surface to the cavity surface. The tensile stress strives to pull atoms from the cavity surface to the external surface. The outcome—the cavity shrinks or enlarges—is determined by the competition between the surface tension and the tensile stress. We next express the ideas in mathematical terms.

Take the solid without the cavity but under the same applied stress as the ground state. Set the free energy to be zero in this ground state. The current state has a cavity of radius R. Let γ be the surface tension (i.e., the surface energy per unit area). In creating the cavity, a surface of area $A = 4\pi R^2$ is exposed, raising the free energy of the system by γA. At the same time, atoms occupying the volume $V = 4\pi R^3 / 3$ move from the cavity surface to the external surface, reducing the free energy of the system by σV. Thus, the free energy of the system, relative to that of the solid with no cavity, is

$$G(R) = 4\pi R^2\gamma - \frac{4}{3}\pi R^3\sigma .$$

In arriving at this free energy function, we do not explicitly invoke the detailed diffusion process. We only assume that the atoms that occupy the volume of the cavity in the ground state completely relocate to the external surface—that is, atoms do not get trapped inside the lattice.

The free energy as a function of the cavity radius is sketched below.



When $R = 0$, $G = 0$, which is the ground state. When the cavity is small, the surface tension dominates, and the free energy increases as the cavity enlarges. When the cavity is large, the hydrostatic stress dominates, and the free energy decreases as the cavity enlarges. The free energy reaches maximum at R_c. The significance of this maximum is understood as follows. Imagine a cavity of radius R, which is different from R_c. Cavity changes its size to reduce the free energy, G. If $R < R_c$, the cavity will shrink to reduce G. If $R > R_c$, the cavity will enlarge to reduce G. To determine R_c, one sets the first derivative of the potential to be zero

$$\frac{dG}{dR} = 4\pi R(2\gamma - R\sigma) = 0$$

Two solutions are found. The solution $R = 0$ corresponds to a local minimum of G. The second solution

$$\boxed{R_c = 2\gamma / \sigma}$$

corresponds to the maximum which we are looking for. For a solid with surface energy $\gamma = 1$ J/m^2, under constant stress $\sigma = 10^7$ N/m^2, the critical radius is $R_c = 0.2$ μm.

Surface tension is usually determined by its consequence. One can imagine an experiment, based on what we've just described, to determine surface tension by approximately determining the critical radius under a known stress.

The competition between the stress and the surface tension is described by a dimensionless number

$$\boxed{\frac{\sigma R}{\gamma}}$$

The number is a combination of material constant (γ), geometry (R), and load (σ). When this number is large, stress dominates, and the cavity enlarges. When this number is small, the surface tension dominates, and the cavity shrinks. The above model analysis shows that the critical value is 2. This group appears in many problems.

The Energy Barrier

At the critical radius, $R_c = 2\gamma / \sigma$, the free energy reaches the maximum, given by

$$G^* = \frac{16\pi}{3} \frac{\gamma^3}{\sigma^2}.$$

For typical values of the surface energy and stress, this energy is large compared to *kT*. For example, for $\gamma = 1 \mathrm{J/m^2}$ and $\sigma = 1 \mathrm{GPa}$, the energy barrier is $G^* \approx 100 \mathrm{eV}$. Consequently, one does not expect nucleation of cavity by thermal fluctuation. The cavity has to pre-exist, introduced in the preparation of the material. It can either grow or shrink.

Concept Words and Their Meanings in This Problem

system	solid with a cavity
state variable	cavity radius
driving force	external stress, surface tension
free energy	$G(R)$ = internal energy - force $\times$ displacement
energy landscape	plot of the potential energy as a function of state variables
length scales	cavity radius R, ratio of two forces γ/σ

dimensionless group $R\sigma/\gamma$

About Surface Tension

1. For most solids surface tension is on the order of $\gamma \sim 1$ J/m^2.
2. Surface tension is caused by atomic rearrangement on the surface (as compared to the regular lattice in the bulk). The rearrangement is localized to a few atomic layers.
3. Surface tension is slightly affected by the applied stress, temperature, and electric field. Such effects are often neglected in calculations.

Some Surface Energy Driven Processes in Technologies

- Sintering of powers (with or without pressure)
- Diffusion bonding
- Wafer bonding
- Optical contact
- Cold welding (Forrest)

Cavity Growth by Other Mechanisms.

In the above, we discuss the mechanism of atomic diffusion. A cavity can grow by bond stretching (elasticity), but the size change is on the order of elastic strain:

$$\Delta R / R \sim \sigma / E \sim 100\text{MPa} / 100\,\text{GPa} = 10^{-3}$$

A cavity can grow by crystal slip (plasticity). Cavitation limit (Y. Huang, J.W. Hutchinson, V. Tvergaard. Cavitation instabilities in elastic-plastic solids. Journal of the Mechanics and Physics of Solids **39**, 223-241, 1991).

A Cavity in an Elastic Solid

It is not so obvious why elasticity can be ignored for real solids. We look at the problem briefly here. Denote E as Young's modules of a given solid. The potential has an additional term scales with the cavity volume:

$$G(R) = 4\pi R^2\gamma - \frac{4}{3}\pi R^3\sigma - \frac{4}{3}\pi R^3 g\frac{\sigma^2}{E}$$

Here g is a positive dimensionless number of order unity, which should be determined by solving the elastic boundary value problem.

Note that we have put a minus sign in front of g. That is, we believe that the elastic energy will promote cavity growth. We can understand this as follows.

- The reference body has no cavity, but is subject to the stress. The stress field in the reference body is uniform.
- The current body has a cavity, is subject to the hydrostatic stress σ remote from the cavity, and is traction-free at the cavity surface. The atoms that occupied the cavity have been relocated to the external surface. The stress field in the current body is nonuniform, and can be determined by solving the elasticity boundary value problem. We want to calculate the *free energy* difference between the current body and the reference body due to the elastic deformation.
- Introduce an intermediate body with the cavity. The atoms that occupied the cavity have been relocated to the external surface. A hydrostatic tension is applied on both the external and the cavity surfaces. Consequently, the stress state in the body is uniform. All three bodies have the same number of atoms. The intermediate body has the exactly same energy as the reference body.
- Now we relieve the traction at the cavity surface, and rigidly hold the external surface of the intermediate body, so that the body goes to the state of the current body. In this process, the external traction does no work, and the relieving the traction on the cavity surface does a negative work to the body. Consequently, the current body has a lower energy than the intermediate (and the reference) body.

We have established the direction of the driving force. Now let us look at the magnitude. Setting the first derivative of the free energy to be zero, one finds that the critical radius is given by

$$\frac{2\gamma}{\sigma R_c} = 1 + g\frac{\sigma}{E}$$

Elasticity is an additional driving force to enlarge the cavity, but the correction is typically very small. The second term is on the order of the elastic strain, which is typically much less than unity. $E = 10^{11}$ N/m^2, $\sigma/E = 10^{-4}$ -10^{-2}.

Reading

Adamson, A.W. (1990) *Physical Chemistry of Surfaces*, Wiley. Chapter 1 describes phenomena due to surface tension of liquids.