thermodynamics always wins. At least, that’s what I say in my thermo class, sometimes remembering to append, “eventually.” That “eventually” is important — if your grandparents, like mine, cooked soup to boiling, you perhaps had the experience of watching an ice cube dropped into a steaming bowl of soup. It melts, and the temperature equilibrates across the soup-system. While it’s pretty rapid, the squirming and hungry three-year-old-me would tell you quite loudly that it was NOT instantaneous (had I known that word at the time). In my thermodynamics-centric view of cooking, an important component of freshness for many foods is how far from thermal and chemical equilibrium that food is, with the off-the-shelf version a merely OK stand-in for what food-X ought to taste like. The transient behavior of food materials turns out to be la difference between fresh and stale,[1] and one of the most sought after properties to stabilize by food designers.

Flatbreads provide an excellent laboratory for this observation, existing in cultures around the world and sharing some transient properties that illuminate this point. My definition of “flatbread” here is intentionally broad — just about any starchy dough that’s cooked in an aspect ratio where its diameter or length is at least 10x its thickness counts. Think of a time when you’ve had an opportunity to taste a really fresh, hot-off-the-cooking-surface naan / crepe / tortilla / chapati / flapjack / injera / pizza / waffle or one of the 125 others listed in Wikipedia.[2] The fresh flatbread displays a variety of textures and often colors as well. Some or all of the exterior may be browned and crisp, especially at edges or on bubbles that extend from the surface, while the interior is soft, chewy, and often creamy in texture.

The association of the crispness with edges and browned parts is not coincidental. To trigger the sensory feel of “crispy,” a water activity (a_w) of 0.35-0.50 is required[3] (to read more on my absolute favorite food and thermodynamics concept, see the Food For Thought column on edible thermodynamics[4]). Recall that water is a pretty small molecule, and therefore many apparently solid foods like strawberries and steaks are nearly all water from a mole fraction (x_w) or activity (a_w) perspective (a_w > 0.95[5]). The dough or batter from which flatbreads arise usually starts with an a_w of up to 0.99,[6] so getting to “crisp” requires the removal of quite a lot of water. This removal is greatly facilitated by the high temperatures provided by the griddle or oven and the ample surface area of an edge or bubble.

The browning observed in cooking a flatbread is largely from the Maillard reactions — a family of reactions that occurs between proteins and sugars, chiefly at temperatures between 100 °C-180 °C.[6] You’ll note that these temperatures are above the boiling point of water, and even accounting for the non-ideal nature of the solutions involved, you’re down to a relatively low x_w or a_w once a temperature of 180 °C is achieved. The Maillard reactions create a variety of molecules, several of which are the tasty toasty and nutty flavors we associate with browned foods. Note there may also be some caramelization going on, but that’s a separate reaction that happens between sugars and is favored by slightly higher
temperatures starting around 120 °C. Fun fact, most of the time when you’re “caramelizing” a food (onions, meat, pretty much anything but straight-up sugar), you’re actually mostly “Maillard-izing” it. Either way, however, given the temperatures involved, both types of browning occur in a low-water environment. This is why the browned bits on the flatbread tend to be both tasty and crisp.

By contrast, the creamy texture of the interior (and the steam you may see when breaking open a fresh flatbread) indicate that there’s a lot more water in this part of the flatbread (a, of about 0.95, give or take depending on type of bread). And so we have the pleasant experience of that first bite of a truly fresh flatbread that is characterized by dis-equilibrium in a across each bite — a little crispy, a little chewy, a little toasty, a little creamy. Yum!

Fast forward to the next hour, day, or week. The flatbread has been treated well — flash frozen or vacuum packed or popped into the fridge for consuming the next day. Even if we’ve taken great care to ensure that no moisture can get in or out of our system (those hot tortillas went straight into a plastic bag with all of the excess air burped out), all the textures are different. Our flatbread is no longer crispy on the outside, creamy on the inside — it’s got a uniform kind-of-in-between texture throughout, even though the brown spots are still on the surface. It’s fine...but not the amazing combo we had initially. Blame thermodynamics (this is often a good answer in any situation, by the way!) In the quest to minimize free energy, water molecules will tend to move towards equilibrium, where a is uniform everywhere in the substance, raising a for the surface and lowering it in the interior. This leaves the interior less moist and the exterior less crisp. This effect is more pronounced in a flatbread than in a loaf-shaped bread of similar age because, being flat, the characteristic length any given water molecule must move from interior-to-exterior is typically much shorter.

But wait — some, usually commercial, versions of these foods maintain their behavior through storage. How does that happen? Kinetics to the rescue! While thermodynamics will eventually win, food formulations can contain molecules intended to radically slow the movement of water within the food. In Eggo® frozen pancakes, the final ingredient listed is “soy lecithin.” In Mission brand flour tortillas, after the baking soda is “distilled monoglycerides.” And Stonefire® Naan contains “dextrin”. These ingredients all share a mission — they slow migration of water from the interior of their respective flatbreads. Soy lecithin is an emulsifier that aids the suspension and stability of oil and water phases in foods. This has the convenient side effect of greatly slowing water’s migration within the flatbread — even though the driving force points to water moving towards the surface of the bread, the emulsifier effectively puts an oily wall in the middle. Thermo will eventually win, but it takes several times longer for it to do so than in the unemulsified version. Monoglycerides are a weaker emulsifier that arise in the breakdown of fats and oils and act in a similar fashion to the lecithin. Dextrin takes a different route — it’s a relatively short yet very hygroscopic polymer of sugars (a starch). Its action is to trap water in more of a gel than an emulsion, but the overall effect is similar — it takes much longer for water to diffuse out to the surface, keeping the outside somewhat crisp and the inside somewhat creamy in imitation of the fresh-baked flatbread.

So next time a student is struggling with a problem and having difficulty distinguishing concepts of kinetics and thermodynamics, whip them up a fresh waffle or tortilla, and give them a conceptual lesson they can really sink their teeth into!

REFERENCES