

Droplets, Crystals, Glasses

As we have seen, within the coexistence region, the relative fraction of liquid and gas is determined by the amount of latent heat (energy) available for evaporation. We can imagine cooling a gas to just below the condensation temperature at a given pressure. The gas then wants to start forming a liquid.

Nucleation

How does one reach equilibrium as we **cross** a first order phase transition? Under random molecule motions, tiny **droplets** start to form. Let us have a look on the energetics of a droplet as a function of its size. We concentrate on a temperature T just below the condensation temperature T_{cond} . At this point, the free energy of the liquid is lower than that of the gas by an amount of $\Delta f \sim (T_{cond} - T)$, **per unit volume**. On the other hand, one has to pay a price to introduce a **surface** between the liquid and the gas. Due to surface tension, this free energy is proportional to the surface of the droplet, and the free energy of a droplet takes the form

$$\Delta F(L) = -\frac{4\pi}{3}\Delta f L^3 + 4\pi\sigma L^2.$$

In this expression, the (positive) surface term dominates for L small, while the (negative) bulk term wins for L large. The **maximum** free energy cost corresponds to a **critical droplet size**

$$L_c = \frac{2\sigma}{\Delta f},$$

and takes the value

$$\Delta F(L)_{\max} \sim L_c^2.$$

Now, as we supercool the gas the gas molecules perform a random "Brownian" motion inducing density fluctuations. Occasionally, in a small region, a higher density will form - a liquid droplet. What happens next? Well...the system wants to locally restore the equilibrium, and thus to lower the free energy. If the created droplet is too small - smaller than the critical droplet size L_c , the droplet shrinks again and disappears! Only if by chance a sufficiently large droplet is formed of supercritical size, it will continue to grow exponentially fast. Since the supercritical droplets are being created by random thermal

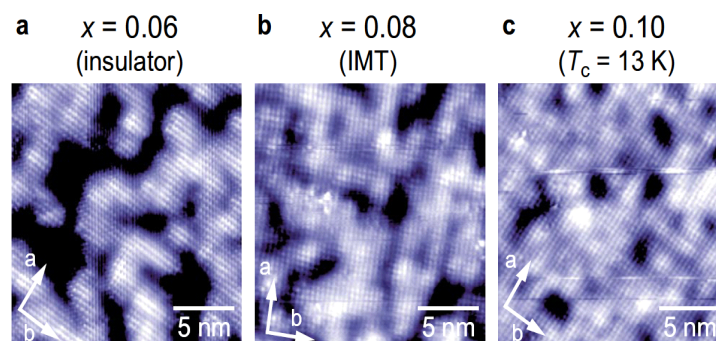
motion, there is a steady rate of creation of such supercritical droplets per unit volume. essentially, the system has to "activate" above the free energy barrier corresponding to the critical droplet, which happens with probability

$$P \sim \exp\{-\Delta F(L)_{\max}/T\}.$$

This process is called **homogeneous nucleation**. In some cases, impurities can act as **nucleation centers**, i.e. they can facilitate formation of droplets. This is why dust and smog can affect the physics of clouds and other atmospheric conditions.

"Quantum Fog" - High Tc cuprates and Neutron Stars

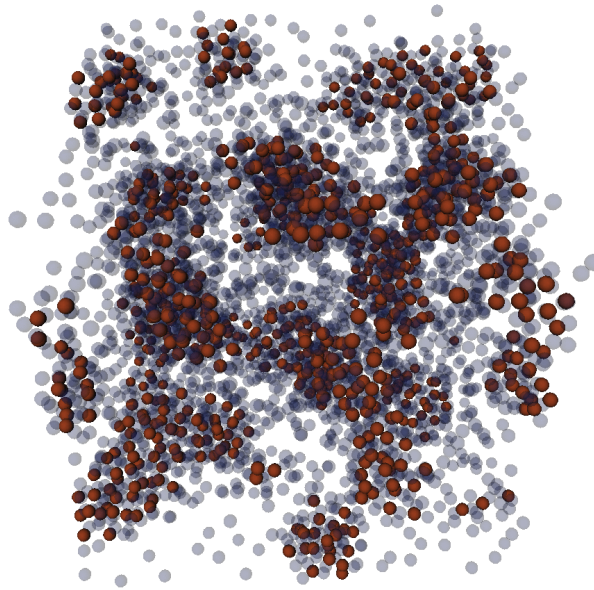
An even more interesting example of inhomogeneous phases emerging due to incomplete ("avoided") phase separation happens in a number of quantum systems. For example, if one wants to fabricate a high Tc material, one dopes an antiferromagnetic insulator such as $LaCuO_4$ by replacing La by Sr . Since Sr has one less valence, it adds an extra hole per dopant. As these added carriers travel around the material they interact with localized Cu spins. The interaction of holes with spin fluctuations is believed to lead to an effective attraction between the holes. As a result the holes would like to "bunch up", i.e. **phase separate**. Note that in electronic systems the density of holes is **fixed by charge neutrality**, so at low doping density one may be "stuck" in the coexistence region! If the holes were



STM imaging: evidence of an inhomogeneous state!
(Takagi, PRL 2004).

charge neutral (as water molecules), then all the holes would go to one end of the sample forming a quantum liquid. But because they are charged, this **violates charge neutrality**.

Global phase separation is thus **FORBIDDEN!** The energy of holes can be still lowered if, instead of global, one achieves a **local (nano-scale) phase separation**. The physics of cuprates is still a hotly debated area of research. But there are many people who believe that this nano-scale phase separation plays a crucial role in determining properties of high Tc materials. These ideas have been first proposed by Lev Gorkov in 1987 just as high Tc was discovered. At present, several people (including myself) at FSU actively investigate the physics of such ”**quantum fog**” phases. Similar behavior is believed to take place in other similar doped oxides: manganites, ruthenates, nickelates...



High Density Neutron Star Matter

Even more interestingly, it is believed that a similar physics takes place in the crust of neutron stars. there, in addition to 90% of neutrons, there are some 10% of protons. The protons tend to attract each other through a strong nuclear force, but they also repel each other by a weaker but long-ranged Coulomb force. As a result, protons form a so-called ”pasta phase” which is believed to play a crucial role in the physics of supernova explosions. This phenomenon is being currently explored at FSU by Prof. Jorge Piekarewicz and his group (see: <http://www.physics.fsu.edu/users/piekarewicz/SantaTecla.pdf>).

Freezing: Crystallization or Glass Formation?

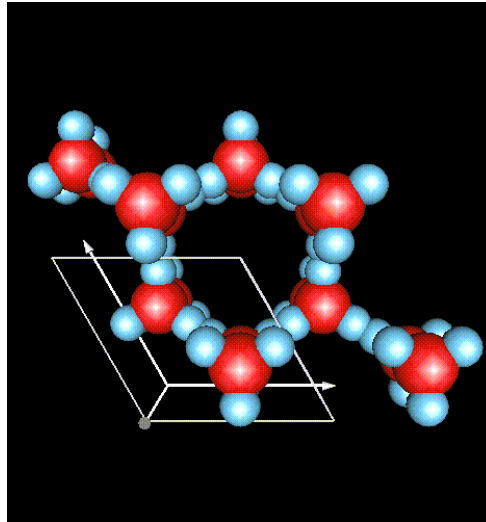
Another example of a first order phase transition is the solid-liquid transition, such as the melting of ice (see: <http://www.its.caltech.edu/~atomic/snowcrystals>). Note, though,



that as the liquid freezes, a microscopic configuration of molecules in the material changes - it assumes an ordered, symmetric arrangements. In contrast to liquids and gasses, or even glasses (amorphous solids), crystals have a special lattice symmetry, by which we can identify them as a different phase. This is our first encounter with a concept of the **symmetry of an order parameter**.

The relative properties of the liquid and the solid may depend dramatically on the symmetry of the crystal. An extreme example is water ice, which has a **lower density** than liquid water (note the slope of the liquid-solid transition line on the phase diagram for water). This is due to the very directional character of hydrogen bonds connecting water molecules in ice. As a result, ice has a very "open structure", i.e. there is a lot of empty space in the crystal - hence its low density. A most dramatic consequence is the fact that ice floats on water, thus "shielding" the lake or river water underneath from the cold atmosphere. This is important for living organisms in the water. For most liquids, the situation is opposite: the liquid has more thermal energy, and hence the molecules stay further apart. A rough estimate of the melting line can be obtained from the **Lindemann criterion**: melting takes place when the amplitude of molecular vibrations in the crystal becomes comparable to the unit cell size.

The crystals grow from the liquid much as the liquid emerges from the gas - by nucleation. However, the crystallization takes place at much lower temperatures, hence the nucleation is also much slower. If one carefully cools the crystal (without shaking it to trigger nucleation), it is often possible to **supercool** water - keep it in the metastable liquid states even below the freezing temperature. Now, the lower the temperature one achieves, the harder it is



to nucleate. Thus, if one can supercool fast enough, one can entirely prevent nucleation of crystals!

What happens in the supercooled liquid as it gets colder and colder? Well...there is less and less thermal energy, and the liquid becomes more and more viscous. The viscosity $\nu(T)$ grows very rapidly with decreasing temperature, and is often fitted to the Vogel-Fulcher law

$$\nu(T) \sim \exp \left\{ \frac{A}{T - T_K} \right\}.$$

Here, T_K is the so-called Kaufmann temperature, where the viscosity seems to diverge, and the liquid becomes a **glass**. But for practical purposes the liquid falls out of equilibrium, and the viscosity becomes too large to be measured, at temperatures $T_G \gg T_K$, which is called the glass transition temperature. Of course, the precise value of T_G depends on the frequency of the measurement - indicating once more that the system is out of equilibrium.

The equilibrium phase transitions such as the evaporation or the crystallization, and even the behavior around the critical point are all well understood. Describing this behavior in detail is the main subject of this course. In contrast, dynamic phase transitions, especially those that take place far from equilibrium are a hot topic of current research. Even more intriguing is the behavior where the glass transition is controlled by quantum fluctuations. Underdoped cuprates, as well as crusts of neutron stars, may very well be examples of such **quantum glasses**. The theoretical description of these fascinating systems is very complicated and subtle, but much progress is being made as we speak (see, for example: <http://journals.aps.org/prb/pdf/10.1103/PhysRevB.72.014536>).